

Molecular Structure and Microstructure of PM_{2.5} Derived from Stationary and Mobile Fossil Fuel Combustion Sources

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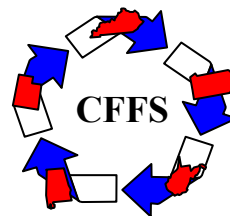
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Abstract: The molecular structure and microstructure of a suite of fine particulate matter (PM) samples produced by the combustion of coal, residual fuel oil, and diesel fuel were investigated by an array of analytical techniques. Some of the results are summarized below.

Diesel PM (DPM): A small diesel engine test facility was used to generate a suite of diesel PM samples from different fuels under engine load and idle conditions. C XANES, ¹³C NMR, XRD, and TGA were in accord that the samples produced under engine load conditions contained more graphitic material than those produced under idle conditions, which contained a larger amount of unburned diesel fuel and lubricating oil. The difference was enhanced by the addition of 5% of oxygenated compounds to the reference fuel. Scanning transmission x-ray micro-spectroscopy (STXM) was able to distinguish particulate regions rich in C=C bonds from regions rich in C-H bonds with a resolution of ~50 nm. The former are presumably representative of more graphitic regions and the latter of regions rich in unburned fuel and oil. The dominant microstructure observed by SEM and TEM consisted of complex chain-like structures of PM globules ~20-100 nm in mean diameter, with a high fractal dimension. High resolution TEM revealed that the graphitic part of the diesel soot consisted of onion-like structures made up of graphene layers. Typically 3-10 graphene layers make up the “onion rings”, with the layer spacing decreasing as the number of layers increases.

ROFA PM: Residual oil fly ash (ROFA) PM has been analyzed by a new approach that combines XAFS spectroscopy with selective leaching procedures. ROFA PM_{2.5} and PM_{2.5+} produced in combustion facilities at the U.S. EPA National Risk Management Research Laboratory (NRML) were analyzed by XAFS before and after leaching with water, acid (1N HCl), and pentane. Both water and acid leaching removed most of the metal sulfates, which were the dominant phase present for most metals (V, Ni, Zn, etc.). This allowed conclusive identification in the leaching residue of important secondary sulfide and oxide phases, including Ni sulfide, a toxic and carcinogenic phase observed in the leached PM_{2.5+} samples. Other significant secondary phases identified included V₂O₄, V sulfide, and NiFe₂O₄.

Coal fly ash (CFA): Leaching produces significant differences in the XAFS spectra for sulfur and arsenic, including the conclusive demonstration of the existence of a minor percentage of the highly toxic oxidation state of As, As(III), in residues of acid-leached samples. To follow up on our observation of last year that significant amounts of Cr⁺⁶ are present in CFA from low-rank western coals, a model western CFA sample was prepared in the Utah combustion laboratory from a Cr-doped western coal. The resulting CFA contained ~0.5 wt.% of Cr⁺⁶ and will be used in future studies to clarify formation mechanisms.

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Summary of CRAEMS program results for year two

Introduction

Numerous studies ⁽¹⁻⁴⁾ have demonstrated a correlation between the concentration of airborne particulate matter (PM) <2.5 μm in mean diameter (PM_{2.5}) and human morbidity and mortality due to cardiovascular disease. As summarized in a recent review ⁽⁵⁾, the combustion of fossil fuels for the generation of electrical power and for transportation is a major source of PM_{2.5}. This investigation is focused on determining the molecular structure and microstructure of combustion aerosols, particularly those derived from coal and petroleum. It has three primary objectives:

1. To identify structural source signatures for PM_{2.5} derived from fossil energy sources.
1. To identify structural features that may be important for human health considerations.
2. To achieve, through laboratory experiments and modeling, a basic understanding of the formation mechanisms of the critical PM_{2.5} structures identified.

The combustion of fossil fuel fuels produces a complex array of PM products. Therefore, we are employing an array of powerful analytical techniques to determine their molecular structure and microstructure. These techniques are briefly summarized below.

- X-ray absorption fine structure (XAFS) spectroscopy provides information on the molecular structure, valence states, and speciation of both major and trace elements.
- Scanning x-ray microspectroscopy (SXM) is used to image and obtain XAFS spectra of individual particles, with a resolution of approximately 50 nm.
- X-ray ray fluorescence (XRF), high-resolution inductively coupled plasma – mass spectrometry (ICP-MS), and instrumental neutron activation analysis (INAA) provide major, minor and trace element concentrations.
- ICP-MS is being used to measure measurement of sulfur isotopic and ratios to determine the percentage of ammonium sulfate in PM_{2.5} derived from different fossil fuels.
- Accelerator MS is being used to investigate the use of ¹⁴C as a marker to distinguish between petrogenic and biogenic sources of carbon in PM_{2.5}.
- Thermal desorption (TD) GC/MS provides information on the structure of volatile

organic compounds.

- ^{13}C NMR and C K-shell XANES are used to determine the molecular and skeletal structure of carbon.
- Computer-controlled scanning electron microscopy (CCSEM) provides particle size distributions (PSD), morphologies, and composition diagrams for particles down to $\sim 0.2\ \mu\text{m}$ in diameter.
- High resolution transmission electron microscopy (HRTEM) and electron energy loss spectroscopy (EELS) is used to investigate the microstructure and molecular structure of ultrafine particles (1 nm - $0.2\ \mu\text{m}$ in diameter).
- Mössbauer spectroscopy provides quantitative iron phase distributions.

These techniques have been used to characterize the structure of variety of combustion PM samples in the second year of this investigation. The results are briefly summarized below.

Summary of second year results

In year one of this CRAEMS investigation, much of our attention was focused on determining the structure of the inorganic PM species formed during fossil fuel combustion. In year two, considerably more emphasis was placed on the investigation of carbonaceous PM. Additionally, a more in depth study of the structure of some of the more critical inorganic PM constituents for health effects and source attribution was undertaken. Some of the more interesting results are for the various categories of PM investigated are briefly summarized below.

Diesel PM:

A suite of six diesel PM samples was generated in a small diesel engine test facility at the University of Utah. The samples were produced with the engine running under either load or idle conditions using a reference diesel fuel and the reference fuel plus 5% of two oxygenate additives. The structure of this suite of diesel PM samples has been thoroughly investigated by a range of different analytical techniques. The principal results obtained for the structural properties of this suite of diesel PM samples are briefly summarized below.

1. Carbon x-ray absorption near edge spectra (XANES) demonstrated that the ratio of graphitic carbon to unburned diesel fuel and lube oil was higher in diesel PM produced when the diesel engine was running under load than under idle conditions. The difference was increased substantially for diesel fuels containing 5% of oxygenate additives, which also significantly reduce the total amount of diesel PM emitted.
2. Scanning x-ray transmission microspectroscopy (STXM) was able to identify carbon with rich in C=C or C-H bonds with a resolution of $\sim 50\ \text{nm}$. The former were associated primarily with graphitic soot and the latter with unburned diesel fuel or lubricating oil.
3. STXM measurements on diesel soot was shown to be capable of distinguishing rich in graphitic soot from regions rich in unburned diesel fuel or lubricating oil with a resolution of $\sim 100\ \text{nm}$.
4. High resolution TEM provides significant insight into the structure of carbonaceous PM emitted from diesel engines. Two significant observations should be emphasized.
 - ◆ Diesel PM exhibits a distinctive microstructure that consists primarily of three dimensional chain-like structures of 20-100 nm primary PM globules.

- ◆ High magnification, high resolution TEM reveals that the primary globules consist of onion-like structures made up of graphene layers. Typically 3-10 graphene layers make up the “onion rings”, with the layer spacing decreasing from approximately 4.5 to 3.4 nm as the number of layers increases.
5. A method of correlating sample conductivity with graphene layering in diesel soot samples was developed. The method relies on measuring a graphite conductance factor from the change in the Q value of an RF coil when a measured amount of sample is placed in the coil. The technique is useful for determining the amount of graphitic carbon in diesel PM. The results correlate well with ^{13}C NMR linewidths and with XRD data.
 6. X-ray diffraction (XRD) established a graphitic crystallite width parameter that correlated well with the graphite conductance factor established by Pugmire and co-workers using ^{13}C NMR.
 7. Small angle x-ray scattering (SAXS) was used to determine several important parameters for diesel soot. These included the mean diameter of the primary diesel particulates, the mean size of diesel PM aggregates, and the fractal dimensions of the diesel PM aggregates.
 8. Thermogravimetric analysis (TGA) results were consistent with the conclusion that the diesel PM consisted of a graphitic soot plus unburned diesel fuel and lubricating oil, and that the latter component was smaller under engine load than under engine idle conditions.
 9. An aromaticity factor for diesel PM was established from the intensity of aliphatic sidebands in the XRD patterns.

Jet PM:

TEM was used to examine PM collected during jet engine tests conducted at the Air Force Research Laboratory (AFRL) at the Wright Patterson Air Force Base. The preliminary results are as follows.

1. With the jet engine running under cruise conditions, chain-like structures of 20-100 nm primary PM globules very similar to the diesel PM are observed. Under idle conditions, larger, more rounded, agglomerates are observed.
2. Attempts to observe graphitic structures at higher magnification were unsuccessful, due to the growth of unusual fibrous carbon structures. Such structures could arise from the volatilization and re-deposition of unburned fuel and lube oil.

Other results for carbonaceous PM:

Upgrades to the small diesel engine test facility at the University of Utah enable better engine control, temperature sensing, air- flow control, and monitoring of brake-specific fuel consumption and horsepower. With this improved engine control installed, a test matrix has been devised that will systematically investigate diesel PM as a function of engine load, cetane number, and fuel composition.

Factor analysis was performed on TD/GC/MS data obtained from PM samples collected along the US/Mexican boarder near Juarez, Mexico and El Paso, Texas. The results show a clear demarcation between high concentrations of PAH's (associated with brick kilns) and animal fatty

acids (associated with cooking) on the Mexican side of the border, and of fossil terpenoids (associated with incomplete combustion of petroleum-derived fuels) plus alcohols and ketones (associated with automotive catalytic converters) on the U.S. side.

Fractal dimension analysis based on SEM or TEM particle shapes appears to be a useful new method to quantitatively characterize carbonaceous particles from combustion sources.

A collaboration has been initiated with the Center for Accelerator Mass Spectrometry to investigate the use of ^{14}C as a marker to distinguish between petrogenic and biogenic sources of carbon in $\text{PM}_{2.5}$.

Inorganic PM constituents derived from fossil fuel combustion:

Significant progress has been made in metal speciation of fine particulate matter from combustion sources. The combination of leaching using aqueous or acid solutions with XAFS spectroscopy has revealed a wealth of information about minor phases present in both residual oil fly ash (ROFA) and coal fly ash (CFA) PM samples. These studies have significantly augmented our earlier studies based solely on XAFS examination of the original bulk material. Some conclusions are listed below for the different types of materials investigated.

It has shown conclusively that sulfates are the dominant form of occurrence of most metals in ROFA PM and that most metals exhibit minor sulfide and oxide occurrences. The major exceptions to this overall scheme are (i) iron, which appears not to form significant sulfates; and (ii) base metals such as lead and copper, which appear not to form oxides. The sulfide occurrences constitute a higher fraction of the metal in the coarse ($>2.5\ \mu\text{m}$) PM fractions compared to the fine ($<2.5\ \mu\text{m}$) PM fractions. In contrast, oxide phases tend to be found only in the finest $\text{PM} < 2.5\ \mu\text{m}$ fractions. We suspect that these differences relate to the combustion process and that the oxide is formed as burn-out goes closer to completion, whereas sulfide is preserved in the more carbon-rich coarser particulate. It is worth noting that at least one of the sulfides identified, Ni sulfide, is a toxic compound.

The combination of leaching and XAFS spectroscopy is less revealing for the CFA PM samples than for the ROFA PM samples. Nevertheless, leaching produces significant differences for sulfur and arsenic, including the conclusive demonstration of the existence of a minor percentage of the highly toxic oxidation state of As, As(III), in residues of acid-leached samples. For metals, leaching is less effective because they are present as aluminosilicates, aluminosilicate glass, or oxides, none of which are significantly affected by aqueous leaching treatments and only slightly so by acidic (1N HCl) treatments.

The University of Utah combustion test facilities have been used to generate samples for the analytical groups to determine 1. the impact of combustion conditions and additives on the emissions from diesel engines, 2. the emission of ultrafine particles from combustion of coal in boilers and gasifier, and 3. the change in size and composition of fly ash when biomass is co-fired with natural gas in lieu of coal.

As we reported last year, flyash from western U.S. coals contains significantly more Cr^{+6} than flyash from eastern U.S. coals [7]. In order to understand this phenomenon, a model CFA has been by combusting a Cr-doped western coal from the Wyodak seam in a drop-tube furnace at the Utah combustion laboratory. Cr XAFS measurements on the resulting samples show that approximately half of the Cr in the CFA PM samples is present as Cr^{+6} , which means that these samples contain ~ 0.5 wt.% of Cr^{+6} . CCSEM and scanning x-ray microspectroscopy (SXM) measurements will be carried out on these samples in the near future to determine the structure of the Cr^{+6} phase.

Combustion experiments were conducted on several coals in a drop-tube furnace with 50% oxygen and variable CO_2 concentration. XRF analysis of the submicron ash demonstrated that CO_2 suppresses vaporization of silica, calcium, aluminum, and manganese, which are likely to form oxides versus other forms and exhibit the CO_2 effect. The CO_2 effect was not evident in the concentrations of potassium, lead, magnesium, sodium, chromium, and iron. XAFS measurements have been initiated on some of these CFA samples.

CCSEM analyses have been performed on CFA $\text{PM}_{2.5}$ and $\text{PM}_{2.5+}$ samples produced by the combustion of four western coals (two subbituminous, one lignite, and one bituminous) and three eastern coals (all bituminous). The results are summarized below.

1. Particle size distributions (PSD) establish that particles with mean diameter $< 2.5\mu\text{m}$ constitute 80-95% of the total number of particles, whereas particles with mean diameter $> 2.5\mu\text{m}$ constitute 80-95% of the total particle volume for both $\text{PM}_{2.5}$ and $\text{PM}_{2.5+}$ samples. The number PSD maxima lie in either $<1\mu\text{m}$ or $1-2.5\mu\text{m}$ size ranges for both $\text{PM}_{2.5+}$ and $\text{PM}_{2.5}$ samples, while that of the volume distributions lies in the $10-40\mu\text{m}$ size ranges for $\text{PM}_{2.5+}$ samples and the $2.5-10\mu\text{m}$ size ranges for $\text{PM}_{2.5}$ samples.
2. Volume percentage-ternary phase diagrams generated from CCSEM EDX compositional data appear to be useful for source attribution. Western/low rank CFA PM are dominated by Ca-aluminosilicate phases, while eastern/bituminous CFA PM exhibit significant amounts of Fe-aluminosilicates. The resulting ternary Ca-Si-Al and Fe-Si-Al diagrams exhibit distinctive composition ranges and Si:Al ratios.
3. Alkali aluminosilicates also appear useful for source attribution. Na-Si-Al diagrams are distinctive for western/low rank CFA PM, while K-Si-Al provides a fingerprint for eastern/bituminous CFA PM.

One of the primary goals of this CRAEMS project is to develop new and better source signature variables that can be used to identify source emissions. For example, most source-receptor models assign the sulfate observed in ambient particulate to sulfur dioxide produced by coal combustion or emitted from vehicle exhaust. This model may, however, be overestimating the contribution of fossil fuel to the sulfate component of ambient particulate. We have developed a method for determining sulfur isotope ratios and are now investigating the possibility of combining isotope ratio data with trace-element and mode-of-occurrence data to determine what fraction of the sulfate in $\text{PM}_{2.5}$ originates from coal combustion versus, for example, combustion of fossil fuels for transportation.

Since lead was removed from gasoline, there has not been an adequate elemental signature for gasoline vehicle emissions and researchers have had to rely upon challenging and lengthy organic compound analysis. We have developed analytical methods for measuring the platinum

group elements in fine air particulate samples and are working with Environment Canada to investigate how this source signature varies from in-use light duty gasoline motor vehicles.

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Investigations of diesel particulate matter using a variety of analytical x-ray techniques

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Introduction

We have investigated the structure of a suite of diesel soot samples prepared in the combustion laboratory at the University of Utah. The samples were generated by a small diesel test engine under idle and load conditions, using one reference diesel fuel and two diesel fuels that consisted of the reference fuel plus 5% of oxygenate additives [1]. We have subjected those samples to extensive analyses using traditional analytical techniques as well as state-of-the-art synchrotron radiation experiments at the National Synchrotron Light Source at Brookhaven National Laboratory and the Advanced Photon Source at Argonne National Laboratory. The techniques included x-ray diffraction (XRD), x-ray absorption fine structure (XAFS) spectroscopy, scanning transmission x-ray microspectroscopy (STXM), small angle x-ray scattering (SAXS), thermogravimetry analysis (TGA), and light scattering. Additionally, Naresh Shah and Yuanzhi Chen of our group have carried out extensive electron microscopy analyses of the samples and the results are reported in a separate section of this report.

For all the techniques mentioned above, significant differences in the sample characteristics were found between idle and load soot, provided that the fuel was oxygenated. For standard diesel fuel, only small differences were found. The differences in structure are summarized in the remainder of this report.

While nearly all of the experiments planned for this suite of six diesel soot samples have been successfully completed, detailed analysis of some of the data is still in progress. Nevertheless, partial results of this work have been summarized in a two papers and several presentations listed below. Several additional papers are in preparation.

1. A. Braun, N. Shah, F.E. Huggins, S. Wirick, K. Kelly, C. Jacobsen, A. Sarofim, G.P. Huffman, "Studies of Diesel PM with X-ray Spectro-Microscopy", submitted to the American Chemical Society journal, Environmental Science & Technology.
2. A. Braun, N. Shah, F. E. Huggins, S. Wirick, K. Kelly, Ch. Jacobsen, A. Sarofim, G. E. Huffman. *Investigations of diesel soot with scanning transmission X-ray spectro-microscopy*. Presented at the ACS Fall Meeting 2002, Boston, and published in the *ACS Division of Fuel Chemistry Preprints*, 47(2) (2002) 627-628.
3. A. Braun, N. Shah, F.E. Huggins, S. Wirick, K. Kelly, C. Jacobsen, A. Sarofim, G.P. Huffman, "Investigation of Fine Particulate Matter from a Diesel Engine using Scanning Transmission X-ray Microspectroscopy", presented at the SES II Meeting at Argonne National Laboratory, May 2002. An updated version was also presented at the Air Quality III conference, September 2002, in Arlington, VA.

General remarks about the soot samples

The soot samples were provided in amounts of ~100 milligrams each. This is sufficient material for all of the above-mentioned analytical techniques. They are in the form of a black powder, with highly dispersed particles ≤ 1 micron in size. Figure 1 shows a light micrograph of a typical sample.

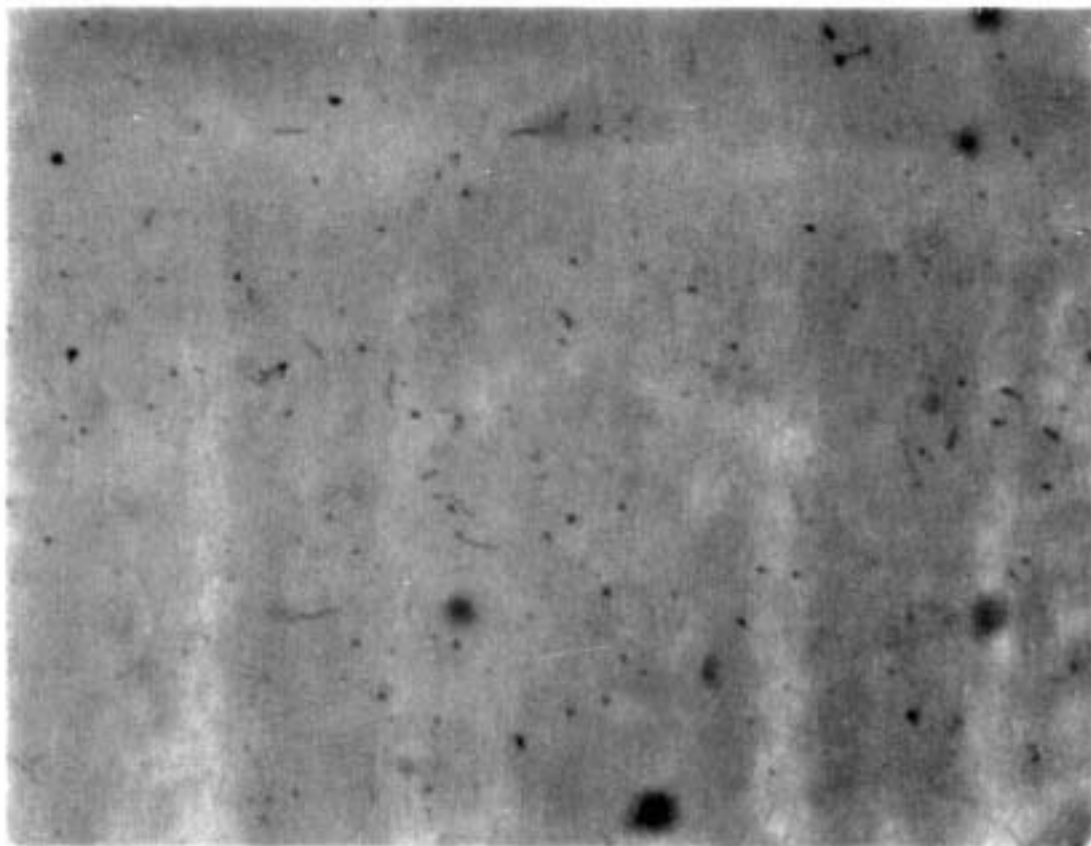


Figure 1: Optical microscopy image of diesel soot (load, not oxygenated). Magnification of 20X.

Soot generated with the engine running under idle conditions will be termed “idle soot” further on, and with the engine running under load conditions, “load soot”. The idle soot sticks together more than the load soot; the particles are more “grippy” or “Velcro-like”. The idle soot is also fluffier than the load soot. We have pressed pellets from the soot to determine their mass densities and found that idle soot has a larger apparent density than load soot. On the other hand, the carbon skeletal density of the idle soots is found to be lower than their corresponding load soot counterparts.

Light Scattering

Light Scattering (LS) experiments were performed by CPS Company for two of our soot samples. The detection and separation power of this technique was enhanced with a disc centrifuge. Results were given as the relative weight (volume fraction)[%] vs. the particle diameter [micron], with the maximum at 110 nanometer for the “idle” soot and 140 nanometer for the “load” soot. Those data were transformed into particle fraction vs. particle radius to obtain average values for particle radius [2, 3].

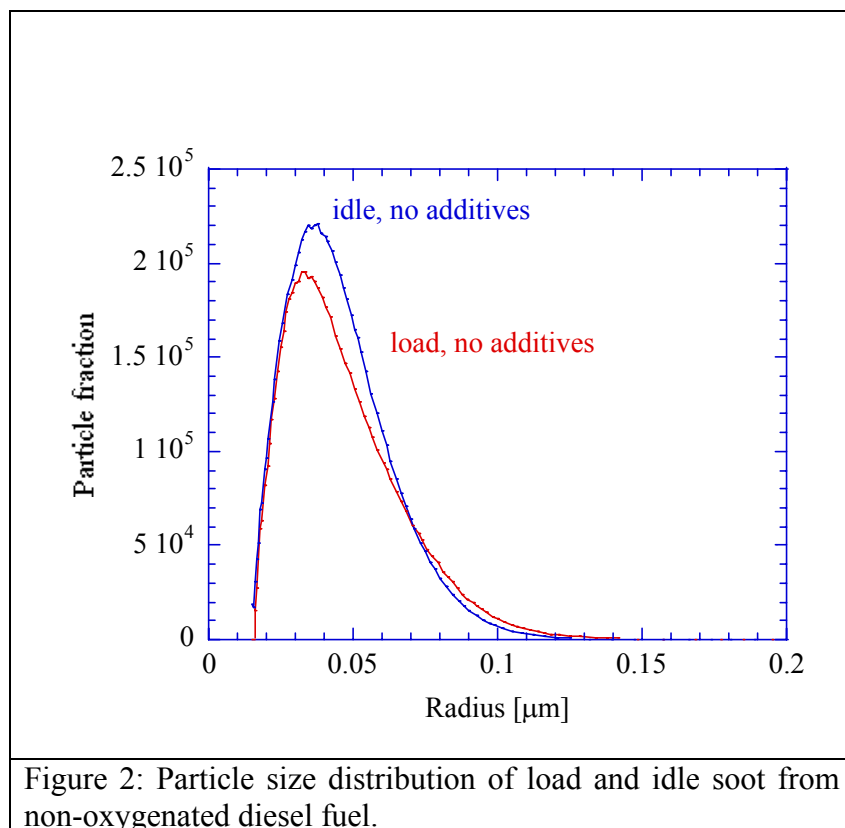


Figure 2: Particle size distribution of load and idle soot from non-oxygenated diesel fuel.

Figure 2 displays the particle size distribution for either soot sample. The particle sizes do not differ significantly from each other. Mean radii were $\langle R \rangle = 45.5$ nm for the load soot, and $\langle R \rangle = 47.2$ nm for the idle soot. For the particle size distribution, we believe that the service company assumed a logarithmic normal size distribution, as can be drawn from the shape and curvature of either distribution in Figure 2.

The LS technique appears to be very suitable for this type of particle size analysis.

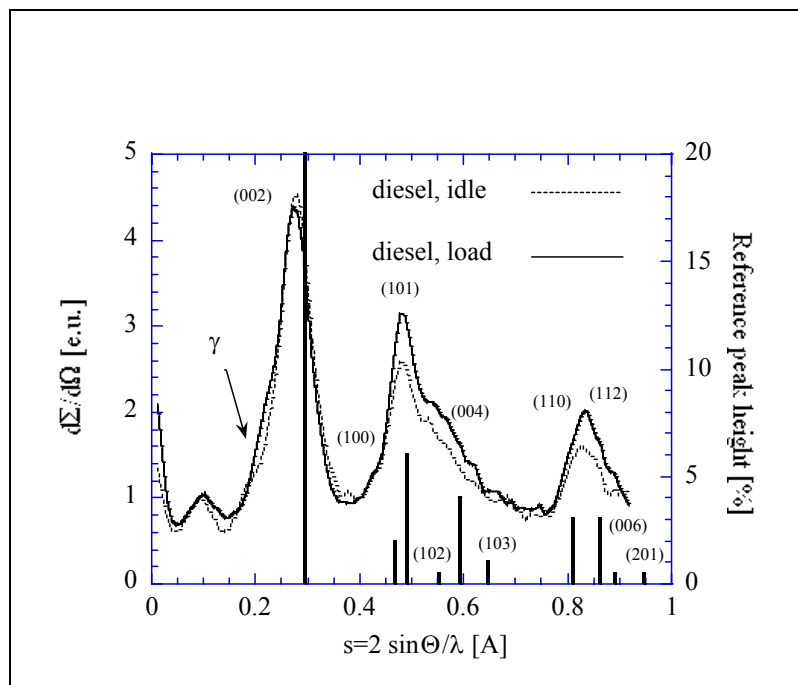
X-ray diffraction

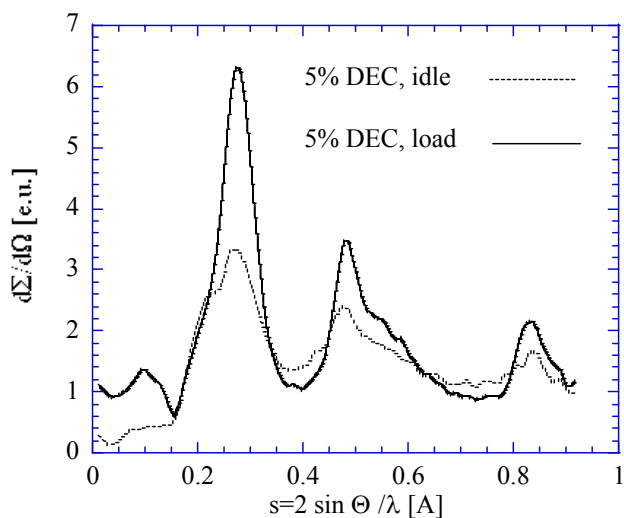
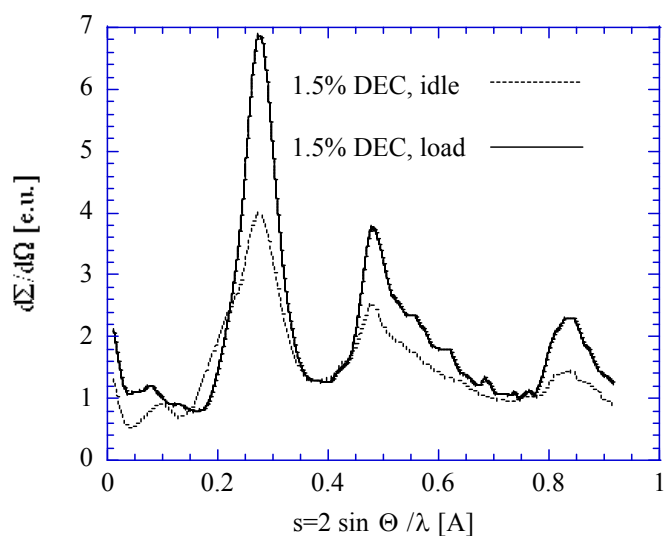
X-ray diffraction (XRD) is usually employed to study materials with long-range order and high crystallinity. Soot is not such a material, but XRD has been employed for many decades in the study of solid carbonaceous matter (i.e. coals), and the literature provides many good research articles on XRD studies of disordered carbons [4, 5].

Unlike totally amorphous materials, poorly ordered carbon samples **do** exhibit Bragg diffraction peaks that allow for an at least semi-quantitative estimation of structural parameters. In this investigation, x-ray diffraction (XRD) was applied in order to find the crystallite size, aromaticity and ratio between aliphatic and aromatic carbon in the diesel soot. Additionally, results on the degree of graphitization as determined by nuclear magnetic resonance by the group of Prof. Pugmire in Utah were confirmed with XRD.

Diffractograms of all six samples were recorded using Cu K-alpha radiation. The soot powders were placed in a standard sample holder. The diffractograms exhibit Bragg reflection patterns (Figure 3) similar to that observed for graphite (2H reference graphite JCPDS 26-1079).

Figure 3 displays X-ray diffractograms in a panel of 3 plots. The left plot, Figure 3.a, compares the soot produced by the reference diesel fuel under idle and under load condition. The most prominent peak is the (002) Bragg reflection, found at $s=0.275$, which corresponds to approximately 26° on the 2Θ scale. The (100) reflection is found at about $s=0.45$. The Bragg reflections of graphite (2H Graphite, JCPDS 41-1487) are plotted as well for reference.





Figures 3a, 3b, and 3c: Comparison of XRD patterns from soot produced from various fuels at idle or load condition.

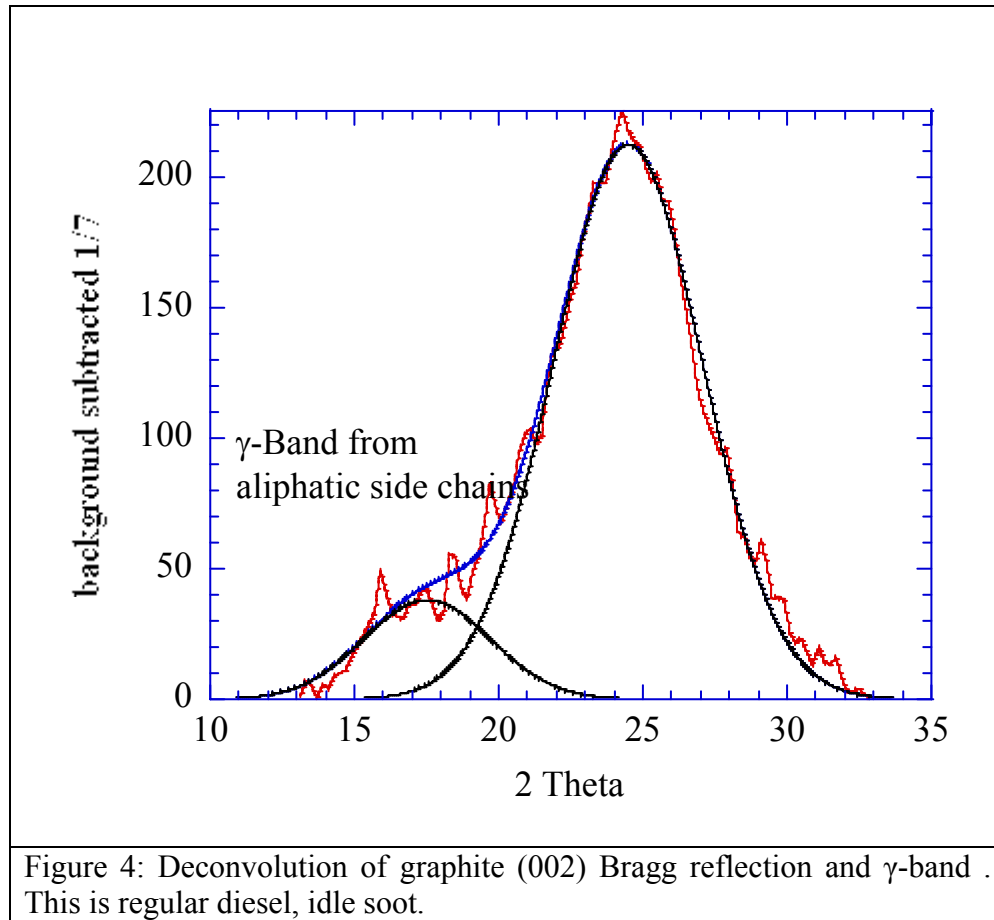
All these reflections are reasonably well resolved, indicating that the soot contains graphite-like material. Idle and load soot sample show diffractograms of overall similar shape, although the idle soot diffractogram peaks are generally broader and weaker than those of the load soots. On the left side of the (002) reflection, the so-called γ -sideband is found at about $s \approx 0.2$. This band is attributed to aliphatic side chains [6]. Figures 3b and 3c show the diffractograms of the idle and load soots obtained from oxygenated diesel fuels (Fig. 3c - the reference fuel + 5% diethyl

carbonate (DEC); and Fig. 3b - the reference fuel + 4.2% ethanol + 1.3% DEC). We note that the full width at half maximum (FWHM) of the (002) reflection is smaller for the load soots, and wider for the idle soots. For the load samples, the intensity of the γ -band seems relatively suppressed, compared to that of the idle samples.

We have fitted the (002) reflection and its γ -sideband with two Gaussian functions in order to determine the aromaticity of the soot by their relative scattering contributions. Figure 4 shows the corresponding peaks of the soot obtained from diesel under idle conditions, as well as the two Gaussian curves and the fit curve. The *aromaticity* can be defined as

$$f_a = \frac{C_{ar}}{C_{ar} + C_{al}} = \frac{A_{(002)}}{A_{(002)} + A_{\gamma}}$$

with $A_{(002)}$ and A_{γ} the areas the two Gaussian curves, which are assumed to be proportional to the number of aromatic and aliphatic carbon atoms per structural unit, C_{ar} and C_{al} , respectively. Table 1 summarizes the results for the aromaticity of the soot.



Visual inspection of the (002) peak positions of either samples as well as the fitting results reveal that the reflections are slightly shifted versus the 2Θ -axis, depending on fuel and operation conditions. We find for the oxygenated fuel that the *load* samples have (002) reflections at higher angles than the *idle* samples.

Fuel type	Aromaticity f of diesel soot		
	regular diesel	diesel +5 % DEC	diesel + 4.2% ethanol + 1.3% DEC
idle	0.868	0.765	0.745
load	0.821	0.930	0.868

Table 1: Aromaticity f of diesel soot as determined by XRD.

The (002) peak position reflects the distance between the graphene sheets. From its width, the crystallite size L_c and L_a were estimated via the Scherrer formula

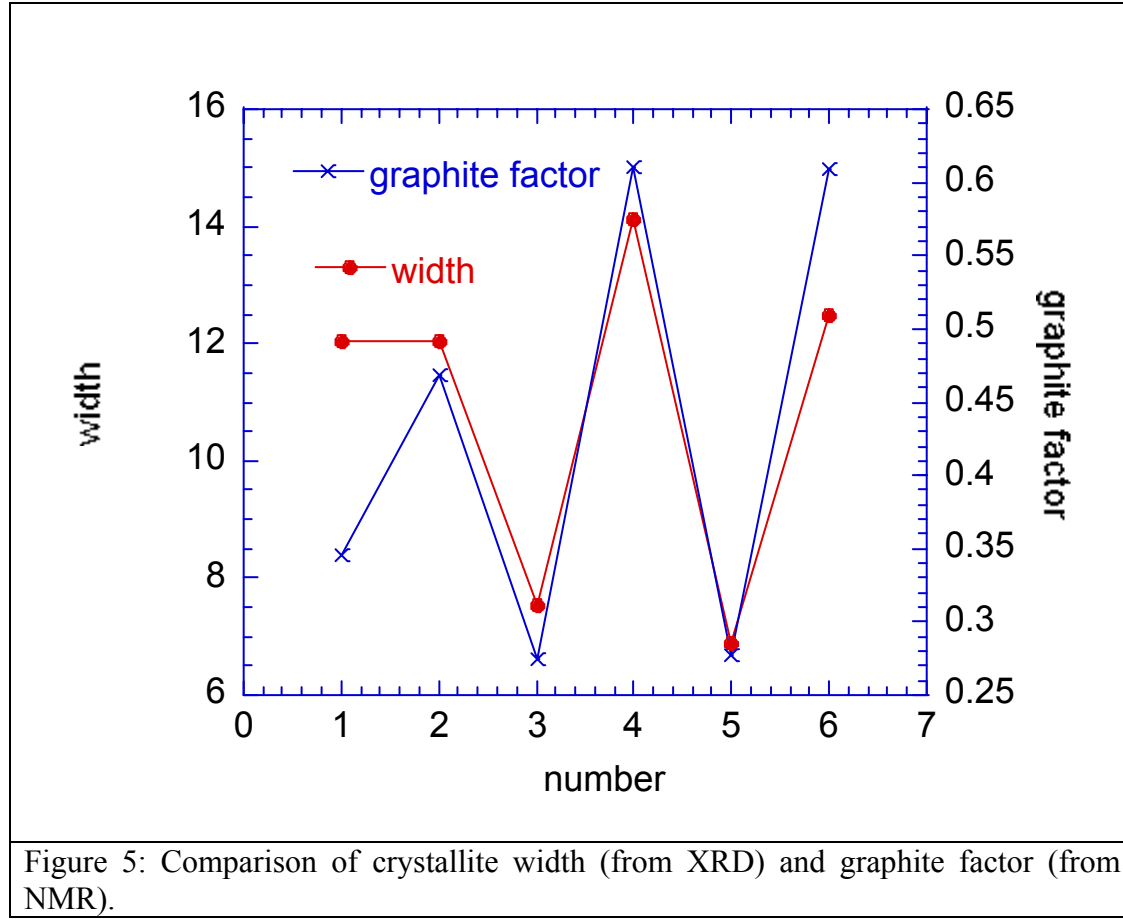
$$w = \frac{0.9 \times \lambda}{b \times \cos(\Theta)}$$

with the X-ray wavelength $\lambda=1.54056$ Å, the peak width b , and the peak position Θ . The empirical parameter b has values between $0.8 < b < 1.9$, where $b = 0.89$ (1.84) is chosen for the (002) reflection and $b = 1.84$ for the (110) and (112) reflections.

Sample	L_c (002) [Å]	L_a (110) [Å]	L_a (112) [Å]
Diesel, idle	11.10	8.67	17.24
Diesel, load	11.78	10.48	16.68
4.2% ethanol +1.3% DEC idle	10.18	6.96	13.24
4.2% ethanol +1.3% DEC load	12.86	8.64	14.92
+5% DEC, idle	8.64	8.93	6.24
+5%DEC, load	10.78	16.30	11.19

Table 2: Comparison of crystallite sizes.

The L_c (002) width of the crystallites correlated well with the graphite factor determined from ^{13}C NMR measurements by the Pugmire group [7], as shown in Figure 5.



Thus, XRD and NMR both verify that diesel soots generated under load conditions are more graphitic than those produced at idle conditions.

We used the x-ray data (d_{002}) to determine the x-ray density of the soot particles, this is, the density of the graphite-like skeleton that neglects the porosity.

$$\rho_x = \frac{3.33538 \text{ \AA}}{d_{002}} \times 2.268 \frac{\text{g}}{\text{cm}^3}.$$

Note that 3.33538 Å is twice the lattice distance of graphite, and 2.268 g/cm³ is the graphite density. The press density was obtained from the weight and dimension of pressed soot pellets.

Figure 6 displays the variation of skeleton density and press density, as obtained by measuring the dimension and weight of pellets. The values of the press density are given in arbitrary units only since no calibration was carried out yet.

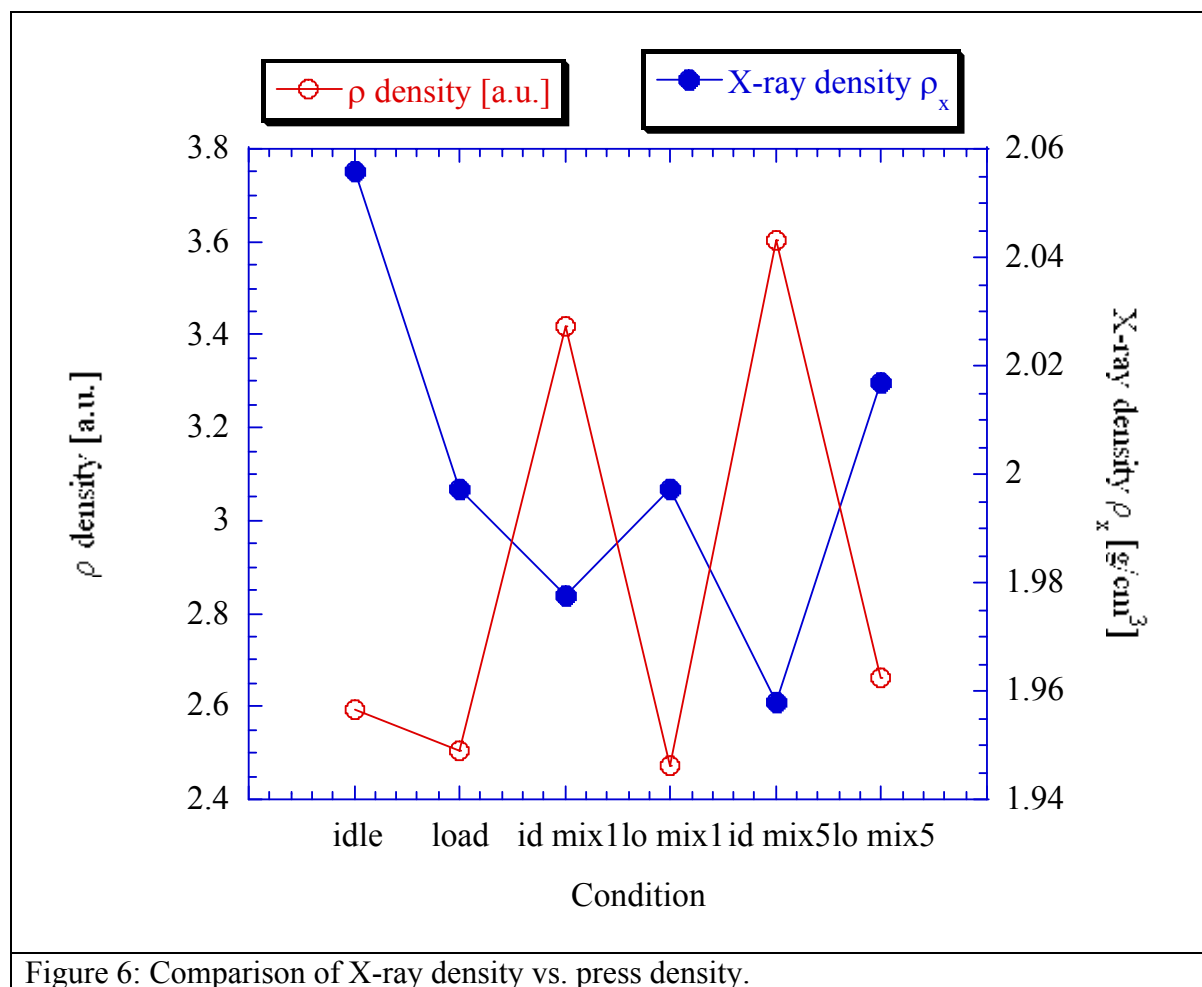


Figure 6: Comparison of X-ray density vs. press density.

Both densities seem to be inversely related. Load soot has a small press density but a high skeleton density, and idle soot has a high press density but a low skeleton density, with the exception of soot from regular diesel.

Scanning Transmission X-ray Microspectroscopy

Using Scanning Transmission X-ray Microspectroscopy (STXM) at Brookhaven National Laboratory, National Synchrotron Light Source, we were able to study single, sub-micron sized soot particles with a spatial resolution of approximately 50 nm. This enabled us to obtain x-ray absorption near edge spectra (XANES) from single soot particles. Characteristic and systematic differences were found for load/idle and oxygenated/conventional diesel soot.

This work was carried out at beamline X1A in collaboration with Christopher Jacobsen and Susan Wirick of the State University of New York (SUNY) at Stonybrook. A detailed discussion of this beamline and of the STXM technique is available at the X1A web site, <http://xray1.physics.sunysb.edu/>. A manuscript summarizing our initial work on diesel PM using STXM has been submitted for publication to Environmental Science and Technology, an American Chemical Society journal [8].

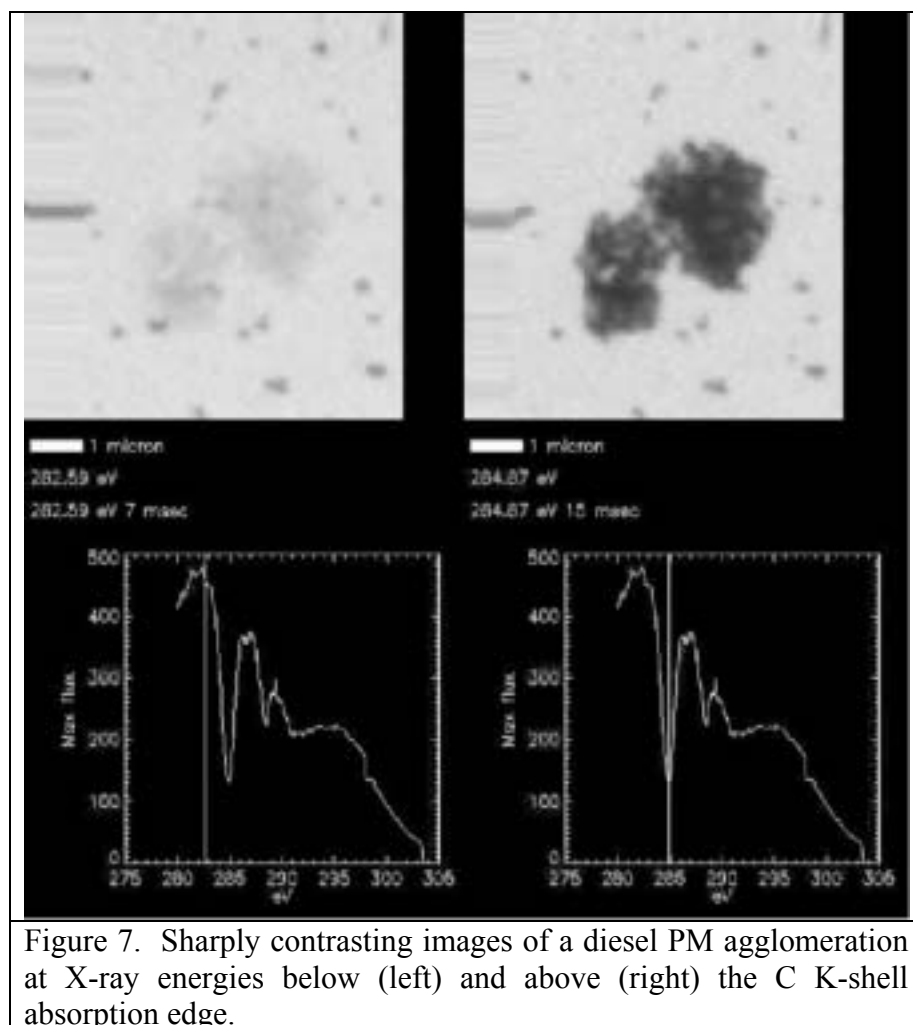
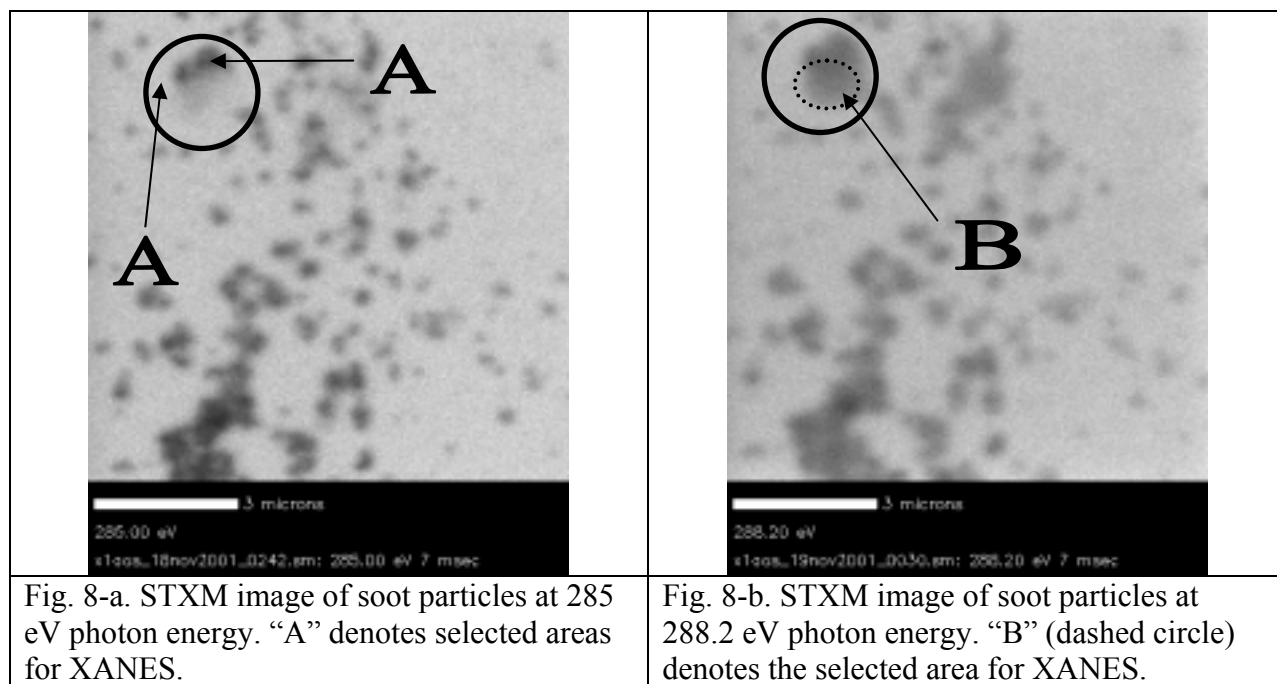


Figure 7. Sharply contrasting images of a diesel PM agglomeration at X-ray energies below (left) and above (right) the C K-shell absorption edge.

Since carbon is quite transparent to the X-ray beam at energies below its K-shell absorption edge, the diesel PM is essentially invisible in images obtained at such energies. A striking example is shown in Figure 7, which shows two images of a four-micron wide agglomeration of diesel soot particles, surrounded by a number of smaller non-carbonaceous particles. The image to the left was scanned below the absorption edge, and the image to the right was scanned above the absorption edge. In the left hand image of Figure 7, only a very faint, diffuse indication of the soot agglomeration can be seen, while the smaller, sub-micron sized non-carbonaceous particles are easily visible. In contrast, the image on the right side shows the particle in the center with clear contrast versus the background, while the smaller non-carbonaceous particles appear the same in both images. Below each image, the transmitted X-ray intensity is plotted versus the X-ray energy. The vertical lines in the plot indicate the energies at which the images were scanned.

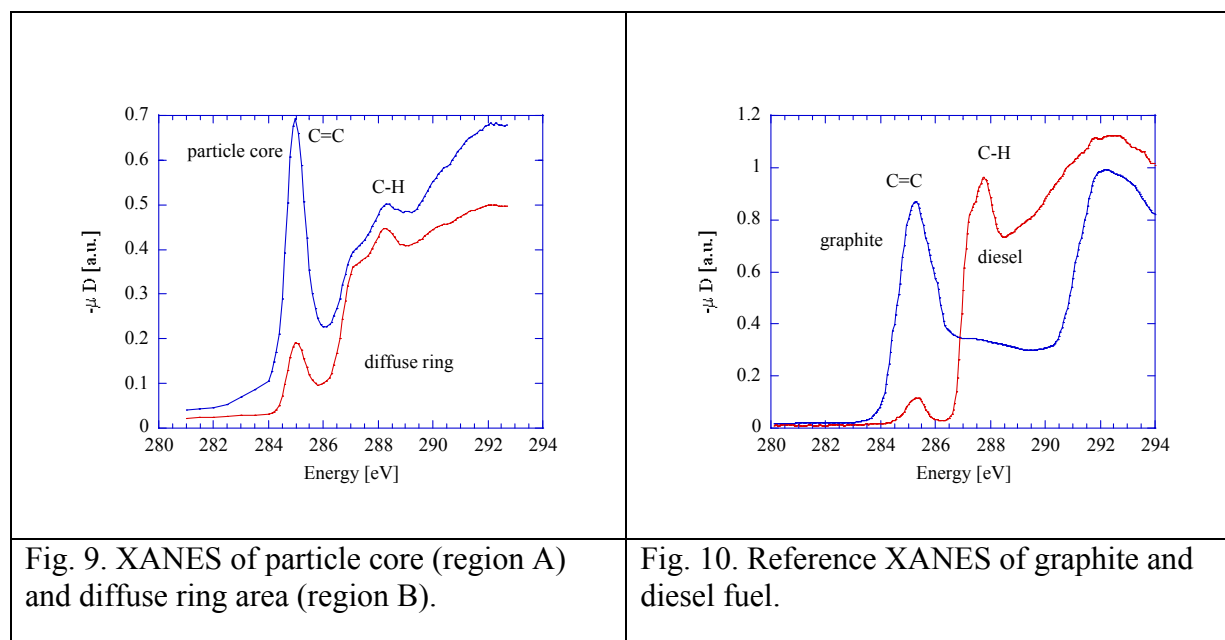
Figure 8 shows two STXM images, obtained from the same sample region at two different X-ray energies. The left image was scanned at a photon energy of 285 eV, and the right image was scanned at 288.2 eV. Both images show the same distribution of particles, dispersed over an area

of about 7.5 x 7.5 microns square. However, the particles on the right image appear more diffuse and spread out then the ones in the left image, which appear smaller and sharper.



In both images, a circle is drawn to highlight a particle agglomeration of two particles indicated by the arrows labeled A with a size of about 0.5 microns each. Both particles are visible in the left image, but not in the right image where only a large diffuse shaded area can be seen. This diffuse region, exclusive the two mentioned particles, is labeled region “B”.

Figure 9 displays XANES spectra recorded from regions A (particle core) and B (diffuse ring). We will focus on the characteristic peaks at 285 eV, 287 and 288 eV. At 285 eV, carbon has a π^* resonance due to C=C bonds. In the vicinity of 288 eV, there are two hydrocarbon resonances, indicative of C-H bonds. Figure 10 shows XANES obtained from the reference diesel fuel and from graphite. On the basis of these XANES, it is logical to conclude that the particle cores (region A) are rich in graphitic carbon, while the diffuse ring region B is rich in unburned diesel fuel and lubricating oil. Although these conclusions are somewhat quantitative, they are supported by the fact that peak intensity ratio between the C=C resonance and the C-H resonance is about 1/10 for the diesel fuel, while the C-H resonance is absent in the graphite XANES spectrum.



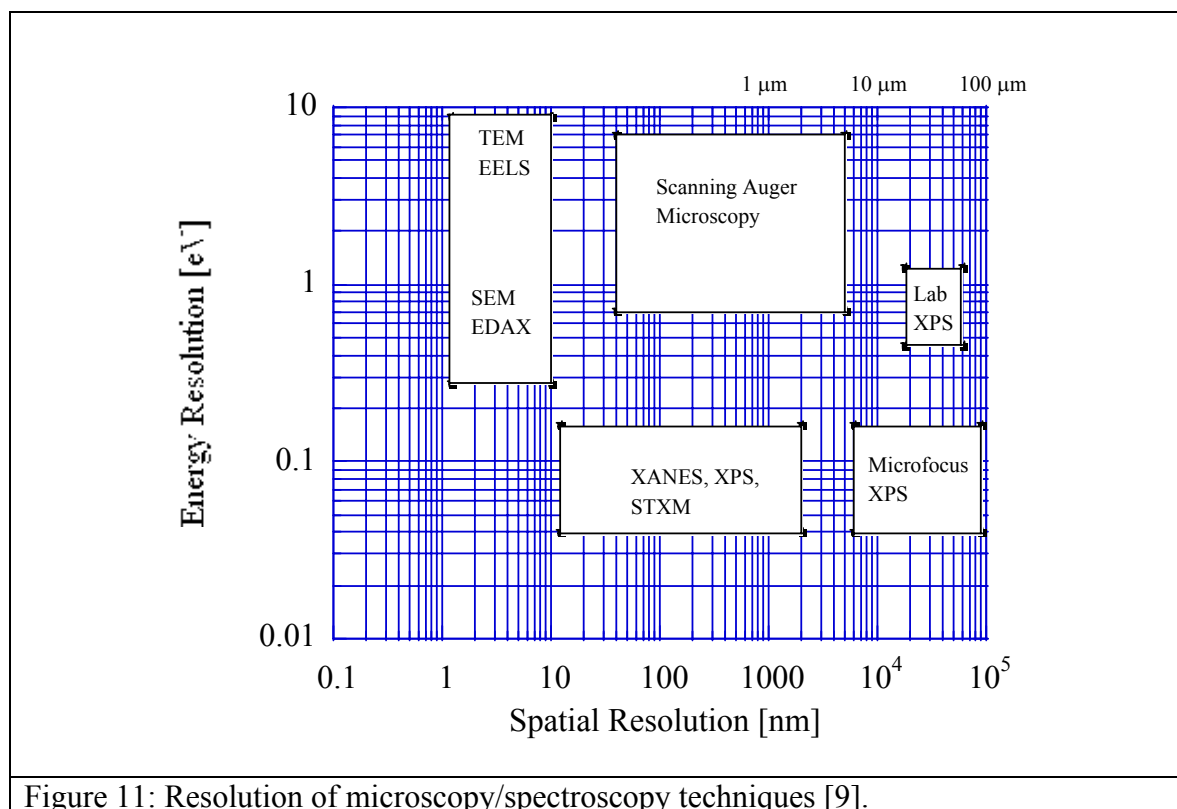
It should be noted that the diffuseness of region B may be due in part to a leaching effect of the acetone used in the sample preparation on diesel fuel and lube oil condensed on the graphitic particle cores.

Efforts to model the diesel PM spectra by building linear combinations of the two reference spectra have not yet been very successful. However, this is probably because we have used only a limited set of reference spectra. It is probable that additional hydrocarbon species are created during fuel combustion.

We have also studied single diesel PM particles and found that different XANES could be assigned to the particle cores and the particle boundary regions. It was found that C=C bonds were dominant in the particle core regions, and C-H resonances in the particle boundary regions. The separation of the two types of region may have been enhanced by the previously noted leaching effect of acetone on diesel fuel and lubricating oil condensed on the graphitic particle cores.

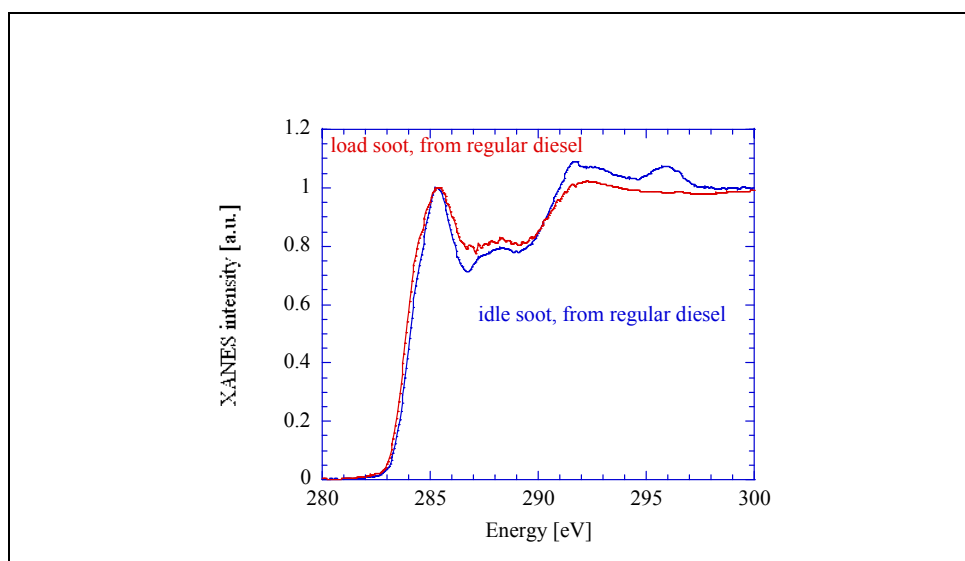
Additional STXM and complimentary experiments are in progress on this suite of diesel soots. A detailed paper will be prepared summarizing the results of these studies.

Finally, it is useful to compare the spatial and energy resolution of various techniques that are being used for PM_{2.5} research. We are using both STXM/XANES and TEM/EELS, which give some similar type of information. Figure 11 compares the resolution of these and other techniques, as of the year 1997. There may have been some improvements in resolution during the intervening years. From our own experiments, we conclude that TEM and SEM still have the best spatial resolution for the morphological characterization, while STXM has clearly the advantage of a better energy resolution as far it concerns the XANES.



X-ray Absorption Near-Edge Spectroscopy (XANES)

XANES were obtained using the STXM microscope as described in the previous subsection. This subsection concerns only results from single-particle analysis, but we plan to carry out future bulk XANES measurements on these soot samples.



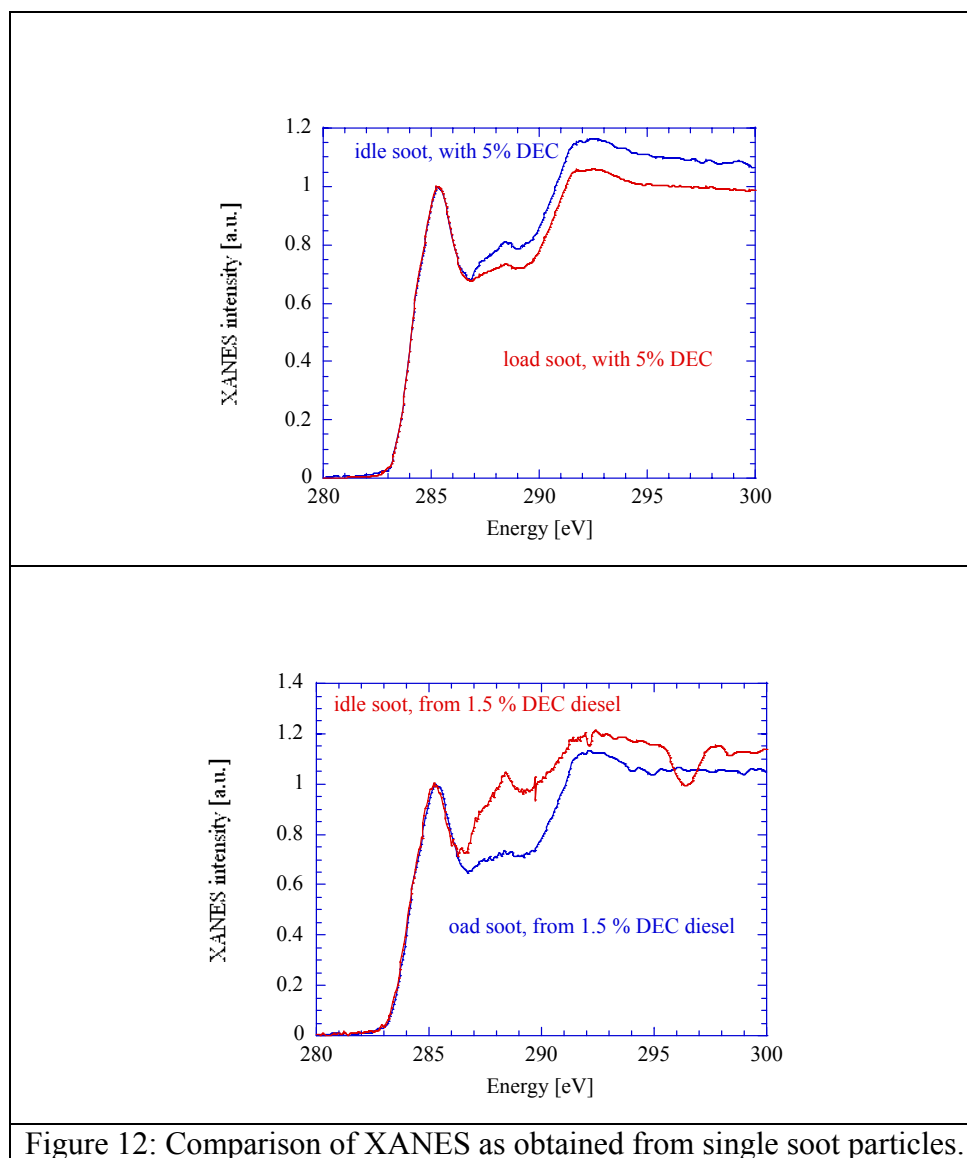


Figure 12: Comparison of XANES as obtained from single soot particles.

A huge body of literature and reference data exists on XANES of carbonaceous samples. Figure 12 displays the XANES spectra of representative particles in the six soot samples. The π^* transitions at 285 eV that are characteristic of carbon-carbon double bonds ($C=C$) are well developed in our samples. Between 287 and 289 eV, there are further transitions, indicative of C-H bonds. The spectra have been normalized to unity at the primary $C=C$ π^* transition peak. While we have not modeled these spectra in detail yet, it is evident that the relative intensities of the C-H resonances to the $C=C$ resonances is higher for the idle soots than it is for the load soots, particularly for the diesel fuels with oxygenate additives. Since the C-H resonances are attributed to unburned diesel fuel and lube oil, and the DEC and ethanol + DEC additives promote more complete combustion of the fuel, this result seems logical. More detailed fitting of the XANES spectra to models is in progress.

Small Angle X-ray Scattering

Small angle x-ray scattering (SAXS) was used to study the soot powder, both in the form of pressed pellets and immersions of soot particles in water and acetone. SAXS is an inelastic scattering technique that focuses on the profile of the (000) (specular) Bragg reflection. Generally, particle size distributions, surface areas and volumes, porosities, and fractal dimensions of objects can be determined with SAXS. We were able to determine the fractal dimension of the soot aggregates and their particle size distribution. SAXS was carried out at two different synchrotron beamlines at the Advanced Photon Source in Argonne National Laboratory, BESSRC-CAT and UNI-CAT.

We were able to resolve three different size ranges in the soot, up to ~ 1 nm, 150-400 nm, and 800 – 1500 nm. This is in agreement with data published in [10]. Objects with size ~ 1 nm are most likely the graphite crystallites that were detected with XRD and observed by TEM. Objects with radii between 150 and 400 nm are the primary particles, as observed with electron microscopy. The large size of 800 – 1500 nm radius must be assigned to agglomerates of the primary particles, also observed with electron microscopy.

SAXS scattering curves are usually plotted in a double logarithmic representation of the scattered intensity versus the scattering vector (“log-log plot”) to obtain a global picture of the structures resolved in the experiment. Figures 13-15 display log-log plots for idle and load soot powder for the three fuels used. Generally, we see a convolution of a power law intensity decay and broad bumps, which account for Bragg-like reflections resulting from a very diffuse coherence length distribution in the particles. The intensity bump in the middle at about $q=0.005$ is a signature from the primary particles. This structural feature is observed in all powder soot samples. While the soot from conventional diesel shows similar scattering curves for idle and load soot, the oxygenated samples show remarkable differences, i.e., for the idle soot samples derived from oxygenated fuels, the bump from the primary particles is overshadowed by the power law decay.

The position of the bump roughly tells us the size of the primary particles (there is a whole body of well established theory for accurate determination), while the power law decay provides information about the fractal dimensions of particle aggregates. Since for the idle soot, the bump is at a smaller q value than for the load soot, load primary particles are smaller than idle primary particles.

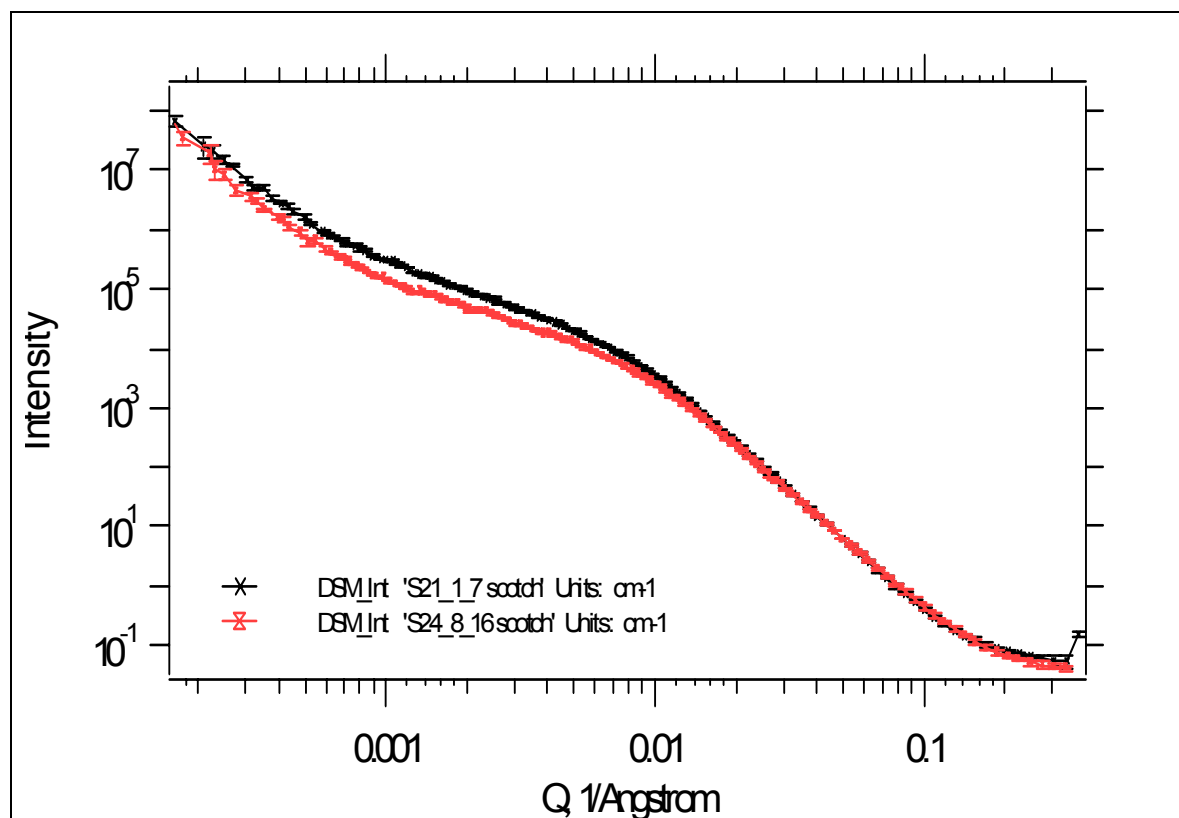


Figure 13: SAXS curves of idle (black) and load (red) soot.

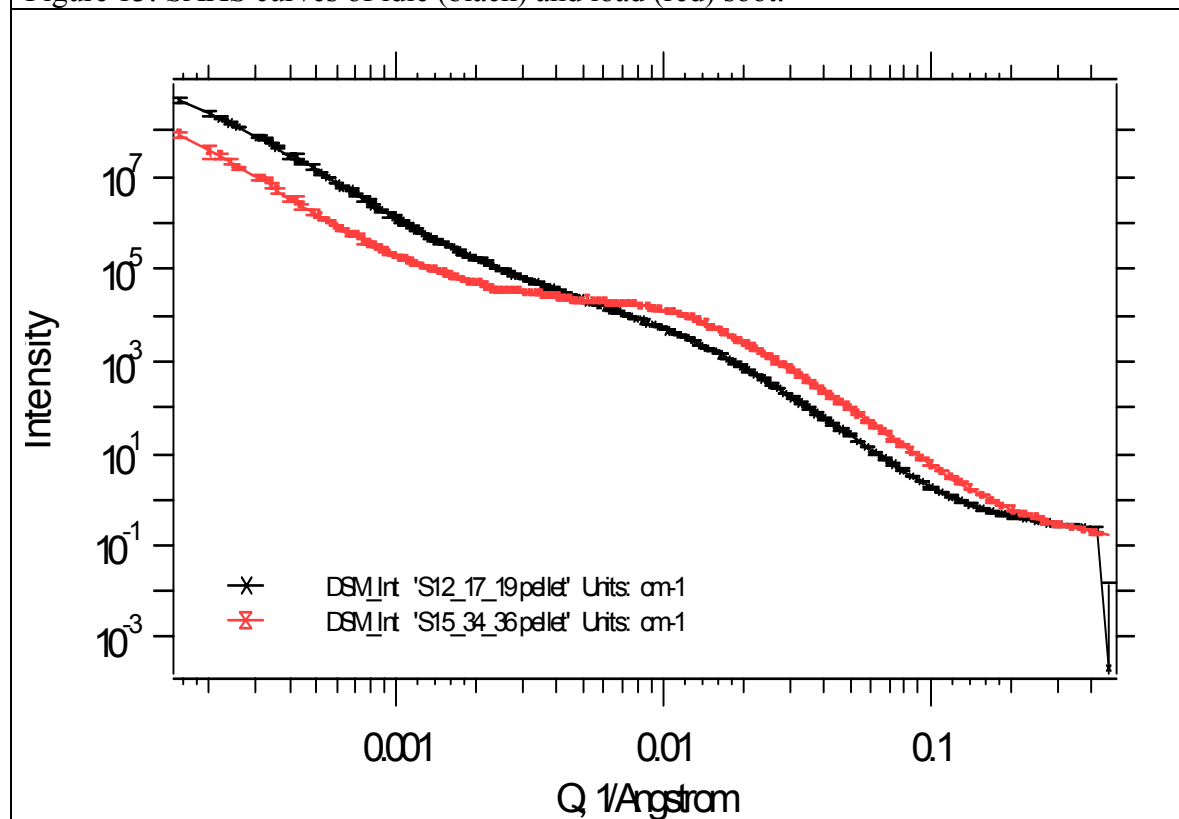
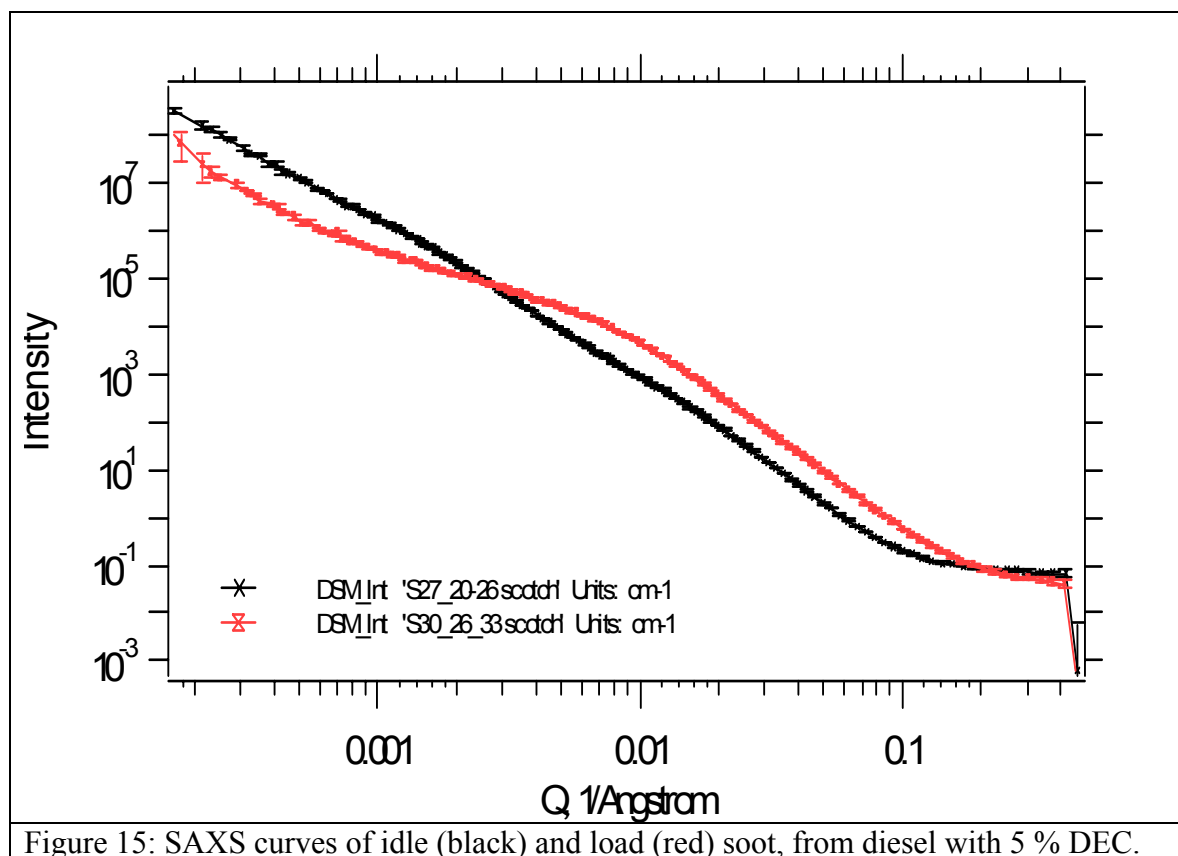


Figure 14: SAXS curves of idle (black) and load (red) soot, from diesel with 1.5 % DEC.



To separate the signal from the aggregates and the primary particles, we used a trick. Pellets were pressed (~10 metric tons load) from the soot powder so that the aggregates became compressed and insignificant compared to primary particle scattering. We also tried suspending the soot samples in acetone and ultra-sonicating as another approach to destroying the aggregates. Figure 16 shows the scattering curves of all samples; loose powders, pressed pellets, and acetone suspensions.

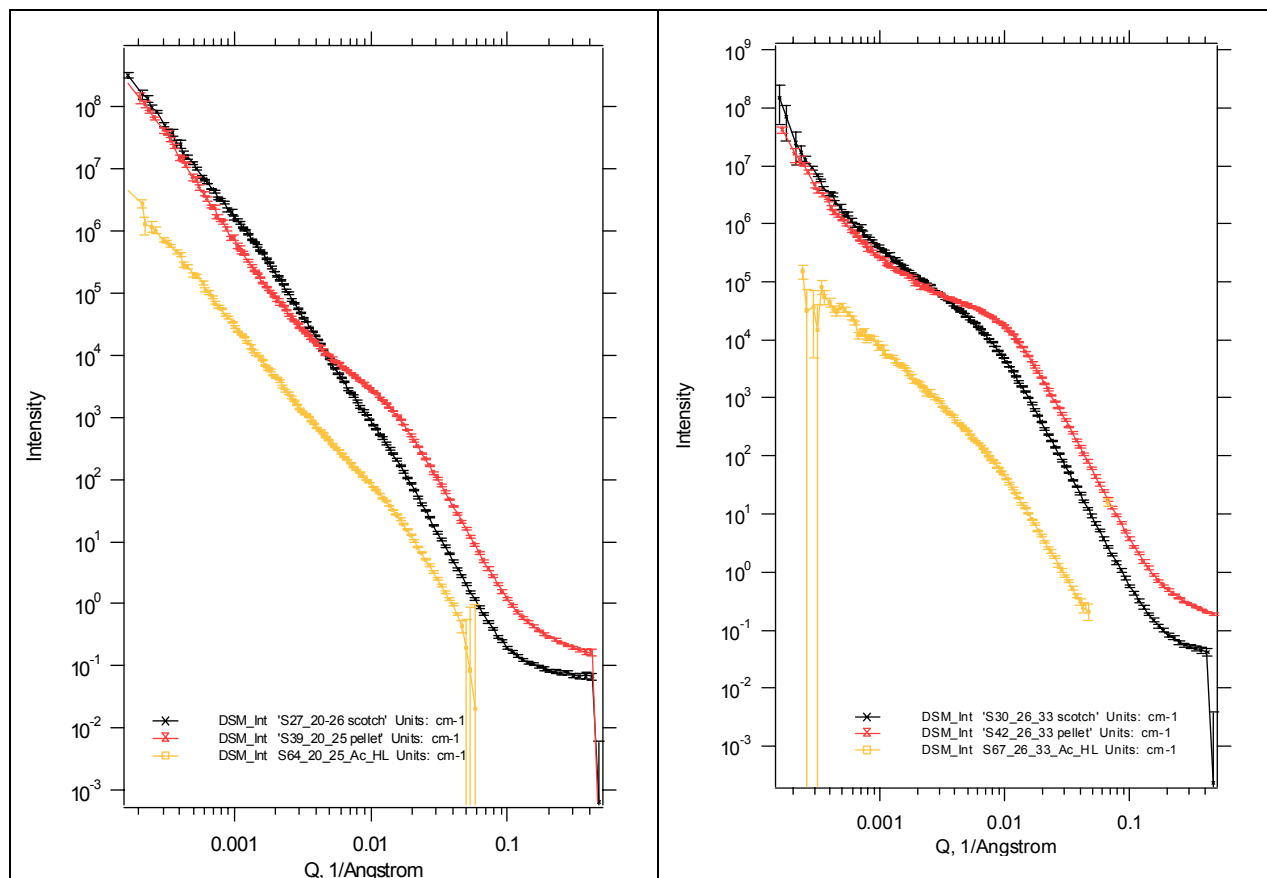


Figure 16: SAXS curves from soot in powder, pellet (curve with higher intensity at high Q values), and immersed in acetone (lower, short curves)).

We have attempted a detailed quantitative analysis by curve fitting this data to conventional SAXS models. In particular, we have determined the particle size and the fractal dimension. For the particle size, we have applied so-called Guinier fits, which give us radius of gyration with respect to the center of electron density of the particles. Assuming one particular particle shape, this can be translated into geometrical dimensions. Here we have assumed that the primary particles are spheres. Examples of the computer fitting procedures and the values obtained from them are shown in Figure 17.

Regarding the fractal dimension, we must distinguish volume/mass fractals and surface fractals. For mass fractals, the mass scales with

$$m \sim R^D$$

and “D” is the fractal dimension, which can be measured by the recording the decay of

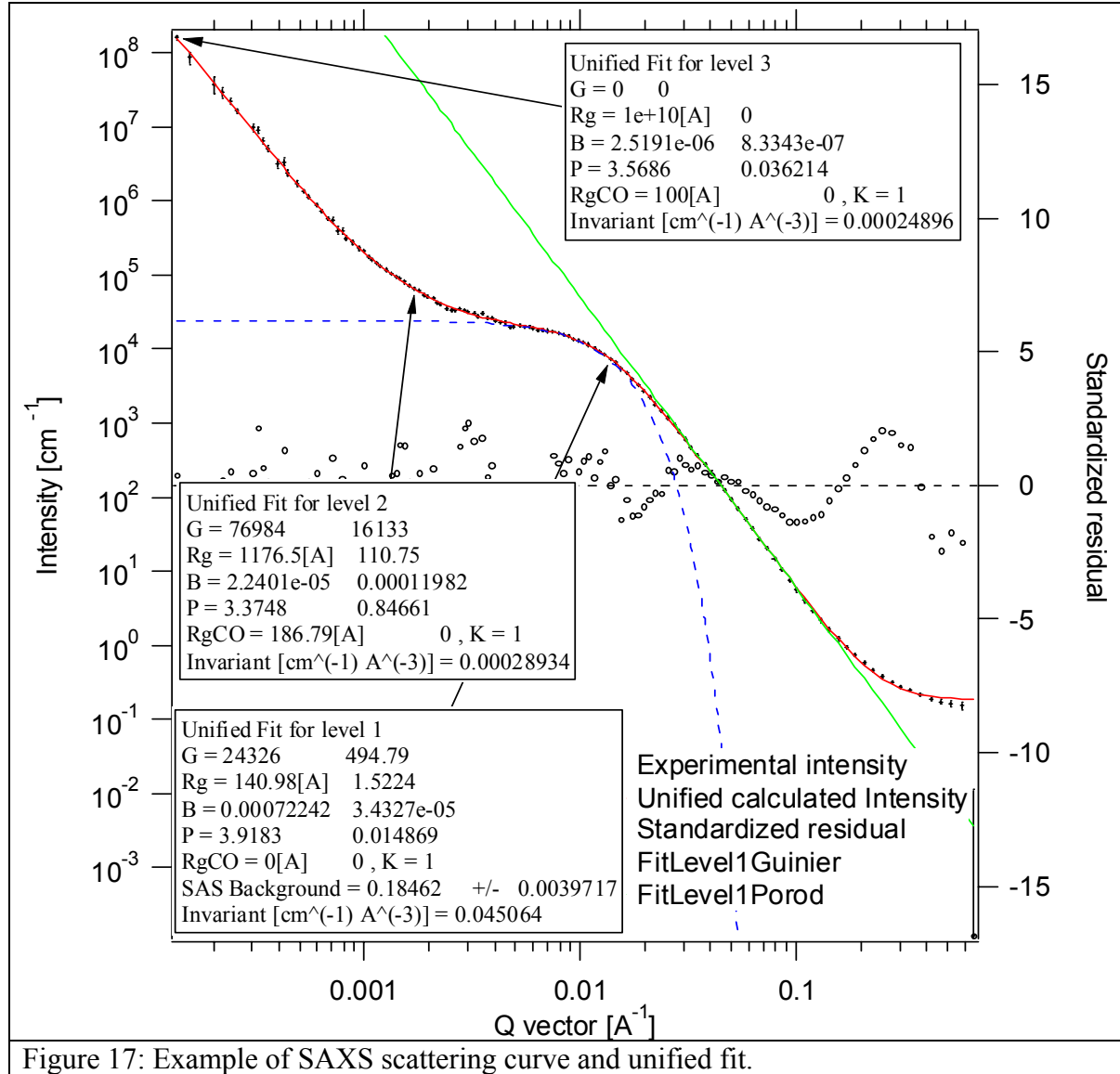


Figure 17: Example of SAXS scattering curve and unified fit.

intensity versus Q . In fact, the exponent of decay “D” can be translated directly into the fractal dimension of the object measured:

$$\frac{d\sigma}{d\Omega}(Q) = NV^2 \Delta\eta^2 Q^{-D}, \quad 1 \leq D < 3$$

For surface fractals, the surface scales with

$$A \sim R^{D_s}$$

and for the intensity variation versus Q we find

$$\frac{d\sigma}{d\Omega}(Q) = NV^2 \Delta \eta^2 Q^{D_s-6} \quad , \quad 2 < D_s < 3$$

For most samples and Q-ranges, the exponent of decay was between -3 and -4, which implies that we have to deal with fractal dimensions between those values. Those are surface fractals; that is, compact objects with rough surfaces.

For large Q, the fractal dimension D_s was found to be in the range between 2 and 2.5. $D_s = 2$ actually means that the surface is smooth, and this is in fact observed more or less for the primary particles.

From SEM/TEM, we will also obtain information about fractal dimension of the soot. We have to bear in mind however that microscopy techniques provide 2-dimensional data with a limited statistical significance, while the scattering results provide 3-dimensional information with a pronounced statistical significance.

Thermogravimetry

Thermogravimetric analysis was performed with a TA 2950 TGA instrument. The program used to analyze our samples was as following: increase temperature at a rate of 20 K/min in N_2 to 100°C and hold for 5 min.; increase at 50 K/min in N_2 to 750°C; hold at 750 °C for 15 min in O_2 . The initial sample amount was always about 20 mg.

Figure 17 provides a typical example of TGA profiles for idle and load diesel soot. The axis for the mass is normalized to unity. On the time axis, the curves are shifted by some minutes to allow the temperature ramp between 100°C and 750°C. Numerical results are summarized in Table 3. We clearly find that idle soot contains more volatile matter than load soot and that the difference is increased by the oxygenate additives.

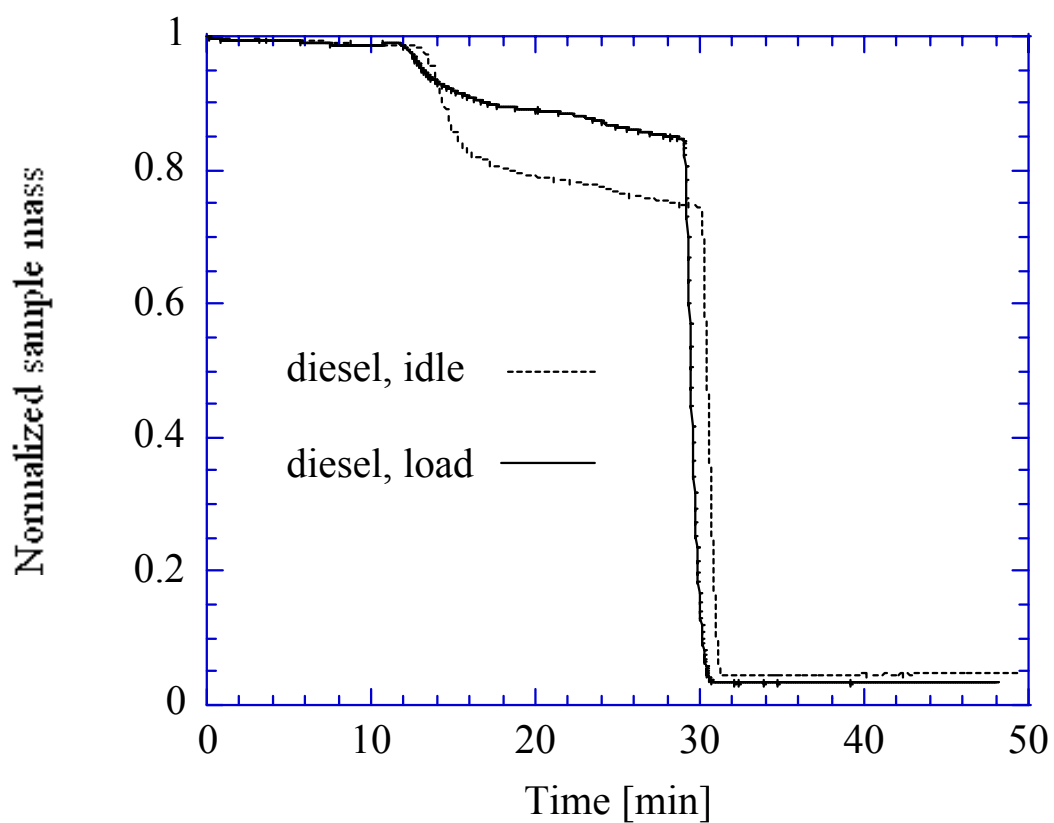


Figure 18: Typical TGA data for idle/load diesel soot samples.

Sample name	Condition	Moisture	Volatile	Residue
1-7	idle	1.757	23.78	4.699
8-16	load	1.145	14.36	3.490
20-25	idle, 4.2% ethanol + 1.3% DEC	1.917	56.19	4.733
26-33	load, 4.2% ethanol + 1.3% DEC	1.375	16.75	2.910
17-19	idle, 5% DEC	2.488	61.80	4.614
34-36	load, 5% DEC	1.025	14.09	2.138

Table 3: Summary of TGA results.

Summary

The principal results obtained for the structural properties of the suite of diesel PM samples investigated in the current study are briefly summarized below.

10. X-ray diffraction (XRD) established a graphitic crystallite width parameter that correlated well with the graphite conductance factor established by Pugmire and co-workers using ^{13}C NMR. An aromaticity factor for diesel PM was established from the intensity of aliphatic sidebands in the XRD patterns.
11. Scanning x-ray transmission microspectroscopy (STXM) was able to identify carbon rich in C=C or C-H bonds with a resolution of ~ 50 nm. The former were associated primarily with graphitic soot and the latter with unburned diesel fuel or lubricating oil.
12. Carbon x-ray absorption near edge spectra (XANES) exhibited a more graphitic signal from diesel PM produced when the diesel engine was running under load than under idle conditions. The difference was enhanced by the addition of oxygenates to the diesel fuel.
13. SAXS results reveal the existence of a threefold size distribution as well as the fractal dimension of the primary particles and larger aggregates. Also, we find that the load soot primary particles are smaller than idle soot primary particles.
14. TGA confirms that idle soot contains more volatiles than load soot does.
15. We generally find that a number of different experimental techniques provide a consistent picture about the difference between diesel soot produced under engine idle or load conditions, using regular or oxygenated fuel.

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New Method for Measuring the Graphite Content of Anthracite Coals and Soots

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Introduction

The amount of graphite-like structure of anthracitic coals and soots is an important parameter for understanding the composition of these materials. The structure of graphite has been studied extensively¹⁻⁶, and is described by the delocalization of the π electrons over the carbon structure. These delocalized π electrons contribute to the conductivity of graphitic material. A recently proposed structure of coals⁷ and soots consists of regions or clusters that are graphite-like in nature, linked by non-conductive chain/bridging regions. The electrical conductivity of these materials will therefore depend on the extent of these graphitic regions. Therefore, by measuring the electrical conductivity of these samples it is possible to estimate the amount of graphitic materials present.

The direct measurement of electrical conductivity is a classical method⁸ in which a pair of electrodes is placed across the sample. However, due to the low resistivity (1.5×10^{-3} ohm-cm),⁹ the resistance of the electrical contact between the electrodes and the sample could seriously affect the measurement results, especially when the sample is a powder. In addition, the heterogeneity of the samples and the presence of nonconductive regions make it difficult to measure the electrical conductivity of the sample in this manner. In order to solve such problems, the method of measuring the quality factor (Q value) of a radio frequency (RF) coil at high frequency has been employed.^{10,11}

A Q meter is used to measure the Q value of a RF coil which is defined by

$$Q = 2\pi fL/R \quad (1)$$

where, f is the applied frequency, R is the resistance of the coil at this frequency, and L is the inductance of the coil. When a sample is placed inside the coil, any conduction electrons in the sample will be driven into motion by the electric field induced by the high frequency magnetic field inside the coil according to the Faraday Law¹².

$$\nabla \times E = -\partial B / \partial t. \quad (2)$$

The interaction of moving electrons with the graphite lattice leads to an energy loss. This energy loss inside a coil results in a decrease in the Q value of the coil and therefore a resultant increase in resistance. The ΔQ between an empty and a sample filled coil is directly proportional to ΔR . Since ΔR is a measure of the delocalized electron content, it is also a reflection of the graphitic carbon content of the sample.

Experimentally, the correlation between ΔQ and the graphitic carbon content can be obtained by performing the measurement on a series of standard samples where pure graphite is diluted with silica gel of known composition. The graphitic carbons content in the unknown sample, i.e., the coal or soot, can then be estimated by determining ΔQ on a sample of known mass.

The Principle of the Measurement

The Q value of an RF coil is measured with a Q meter, a classical electrical instrument.¹³ Let Q_o be the value of the empty coil. The value of Q_o decreases to Q_i when a sample that contains conductive material is placed inside the coil, but the inductance L remains essentially the same (less than 1% change). The energy loss due to the moving conduction electrons interacting with the graphite lattice causes an increase in the resistance from R to $R+\Delta R$ with a corresponding decrease in the quality factor from Q_o to Q_i and

$$Q_i = 2\pi fL/(R+\Delta R). \quad (3)$$

Equation 3 can be rewritten as

$$Q_i = 2\pi fL/R(1+\Delta R/R) = Q_o/(1+\Delta R/R) \quad (4)$$

For the coil used in this study at $f = 100$ MHz, $Q_o = 258$, $L = 0.145\mu H$ and the calculated value of R is 0.353Ω . Substituting these data into equation 4 gives

$$Q_i = 258/(1+\Delta R/0.353\Omega) = 258/(1+\Delta R2.83\Omega^{-1}) \quad (5)$$

A plot Q_i vs ΔR results in a hyperbolic curve with a vertical asymptote at $\Delta R = -0.353\Omega$. Inverting both sides of equation 5 yields the linear relationship

$$1/Q_i = (1+\Delta R2.83\Omega^{-1})/258 = 0.00388 + \Delta R0.011\Omega^{-1} \quad (6)$$

Recognizing that ΔR is much less than 1Ω a Taylor series expansion ($1/(1+x) \cong 1-x$) yields equation 7.

$$Q_i = 258(1-\Delta R2.83\Omega^{-1}) \quad (7)$$

As mentioned earlier ΔR is proportional to the G , the quantity of graphite (mg) in this limited volume of sample. Therefore, G can be represented by

$$G = K\Delta R \quad (8)$$

By obtaining a series of Q_i and ΔR values from a set of samples with known graphite concentration the coefficient K can be obtained and a linear relationship between Q_i and G can be written as

$$Q_i = 258[1-(G/K)2.83\Omega^{-1}] \quad (9) \text{ which can be rearranged to}$$

$$G = -1.37 \times 10^{-3} Q_i K \Omega + 0.353 K \Omega \quad (10)$$

The practical form of equation 10 will be discussed in the next section.

Experimental Details

A Q meter (Type 170A, Boonton Radio Corporation U. S. A.) used for measuring the Q value of a RF coil. The operating frequency used is 100MHz for reasons of convenience, coil size and Q measurement sensitivity. A five-turn solenoid coil of inside diameter 0.83 cm, and length 1.40 cm, wound from 16-swg copper wire was used for the experiments. The inductance of this solenoid coil is $0.145\mu H$ and at 100MHz the Q value is 258.

Each sample was placed in a zirconia solid-state rotor (Chemagnetics, Inc.). In each measurement a constant volume of sample (0.33 cm^3) was used which filled to solenoid. A set of standard samples was prepared by mixing pure graphite powder (Aldrich Catalogue NO: 28286-3) with silica gel (Aldrich Catalogue NO: 28859-4). The value of Q_i is silica gel independent. The standard and test samples occupied the same volume. Care was taken to place the sample in the sample holder such that the entire sample was within the coil for the Q measurement. The mass of each sample was also recorded.

The measurements of the unpaired electron concentration in each sample were made on a Bruker ESR spectrometer. Experimental details of the measurement will be discussed in a subsequent paper. All NMR measurements were obtained on a Chemagnetics CMX-100 spectrometer using a PENCIL rotor spinning system under conditions described previously.¹⁴ All experiments were carried out at room temperature.

Results and Discussion

Table 1 contains the Q_i values associated with the standard samples of varying graphite content. The least squares fit of the data is:

$$G \text{ (mg)} = -0.69917Q_i + 182.30 \quad (11)$$

This is the form of equation (10) and is used to calculate the graphite content of test samples.

The graphite factors in Tables 3 and 4 are the values derived from equation 11 normalized by the weight of the sample.

Four anthracitic coals (LCNN, Jeddo, UAE and Summit) obtained from The Pennsylvania State University were used in this study. The elemental analysis is provided in Table 2. The measured Q_i values, the graphite content, the atomic ratios C/H and the concentration of the unpaired electrons are given in Table 3. Similar information for several soot samples is given in Table 4.

This method has been applied for the first time to measure the graphite-like structures in the anthracites and soot samples. Both of these materials are of complex composition containing mixtures of both amorphous and semi-ordered structures and, as far as the investigators can determine, no data of this type have previously appeared in the literature. However, based on some results from other experiments, a possible qualitative explanation will be discussed as below.

The data in Table 3 indicate that the differences in graphitic carbon content of the four anthracites is significant, i. e., by an order of magnitude when one compares the data of the LCNN and Summit samples. However, the concentration of unpaired electrons in these four samples is essentially constant, varying by less than a factor of 2. The graphite factor in the anthracite sample with the highest concentration of unpaired electrons (UAE) is only 0.024. These results indicate that not all measured unpaired electrons contribute to the electrical conductivity. No change in the Q value of a coil is observed when a stable free radical such as DPPH (a standard free radical sample) is placed in the coil. These data indicate that there are at least two different types of electrons in the systems under study; 1) electrons such as found in DPPH where the electron is localized and, 2) electrons that can occupy conduction bands in graphite type structures made up of extended hexagonal ring systems. These extended ring systems may contain, especially in the soot samples, some five-member rings.¹⁵

It is still not clear what size hexagonal ring systems is large enough to exhibit conduction behavior. For example, coronene, which has seven rings, has no effect on the Q value of the RF coil. Celzard⁷ proposed that at least 70 hexagonal rings and a C/H weight ratio higher than 50 (atomic C/H $\approx$ 4.2) is where conductive behavior starts. According to the data shown in Table 3 the atomic C/H ratio of the anthracite coals from LCNN to Summit is 5.35, 4.44, 3.59, and 3.13, respectively. Comparison of these data with the graphitic carbon content seems to be reasonably in line with the results of Celzard.

The C-13 MAS spectra of four of the samples examined in this study are shown in Figure 1. The spectra of two anthracites and the anthracene soot residue were obtained using the CP technique. The diesel soot spectrum was taken with the single pulse technique due to a depletion of protons in the sample which renders the CP technique ineffective. These four samples have quite

different percentages of the graphitic carbon. The graphite-factors for the four samples are: 0.014, 0.148, 0.48 and 0.61 for Summit, LCNN, the 1400 K anthracene soot residue and diesel soot #4, respectively. One can see that there is a great variation of line widths among the four samples that, to some degree, follows the graphite factor. The increased line width is due to anisotropy of the magnetic susceptibility of regions of graphene layering that is not totally removed under MAS conditions.^{16,17} The Summit sample has the appearance of a normal diamagnetic sample with a very small graphite factor and no unusual line broadening. While the line width (FWHM) of the LCNN is essentially the same as that of the Summit, some line broadening appearing as Lorentzian are evident in the LCNN sample. The anthracene soot residue has even broader wings and the broadening of the main resonance is approximately 40% than that of the LCCN. The diesel engine soot has an extremely broad resonance which is also noted in samples so deficient in proton content that the CP experiment is not effective.¹⁴

Conclusion

A rather simple method seems to be useful for correlating sample conductivity with the presence of graphene layering in graphitic carbon structures in anthracitic coals and numerous soot samples. The technique reported is useful for estimating the amount graphite like structures in amorphous carbonaceous samples. It has been demonstrated that the number of unpaired electrons, per se, may not be a reliable parameter for estimating either sample conductivity or the extent of graphitization of soot samples. By utilizing a radio frequency coil one can induce a high frequency electric field in the sample and thus avoid any physical contact with the sample. This technique renders the experimental results free from any of the classical problems associated with electrical contact at the surface. The data indicate that the concentration of free radicals in the sample is not a reliable indication of either the conductivity of the sample or the amount of graphitic carbon present. High resolution TEM data indicate that different levels of ordered structures exist in many of the samples that we have examined and an analysis of the relationship between structure and conductivity will be attempted.

Table 1. The Q_i value associated the samples with different graphite content.

Sample	Sample Weight (mg)	Graphite Content (mg)	Graphite (%)	Q_i Value ^a
1	181.9	60.3	33.2	182.4
2	185.2	36.5	19.7	199.2
3	167.3	24.2	14.5	222.0
4	177.6	17.2	9.68	242.2
5	182.7	8.6	4.7	248.2
6	193.2	5.8	3.0	252.0
7	193.0	4.2	2.2	254.4

- a) The frequency of the measurement was 100MHZ; at this frequency the Q value of the empty coil is 258.

Table 2. The elemental analyses of the anthracite coal samples.

Sample	C (%)	H (%)	N (%)	S (%)	O (%) (by diff)
LCNN	95.7	1.5	1.2	0.5	1.0
Jeddo	95.2	1.8	1.1	0.6	1.3
UAE	94.0	2.2	1.0	0.5	2.3
Summit	93.2	2.5	1.6	0.6	2.2

Table 3. The measured graphite-factor, C/H atomic and mass ratios, Q_i measurement, and spin concentration of unpaired electrons of the anthracite coal samples.

Sample	Graphite Factor	Atomic C/H	C/H Weight Ratio	Q_i Value ^a	Spin Concentration (10^{19} spins/g)
LCNN	0.148	5.35	63.8	184	3.3
Jeddo	0.112	4.44	52.9	200	3.5
UAE	0.024	3.59	42.7	250	4.9
Summit	0.014	3.13	37.3	254	2.6

a) The frequency of the measurement was 100MHz; at this frequency the Q value of the empty coil is 258.

Table 4. The measured graphite-factor and unpaired electron spin concentration of some soot samples.

Sample	Sample Weight (mg)	Graphite Factor	Q_i Value ^a	Spin Concentration (10^{19} spins/g)
Anthracene 1400 K Soot Residue	163	0.48	148.8	11.00
Diesel Soot Residue ^b	192	0.43	143.0	0.87
Ethylene Soot Residue ^b	150	0.48	157.0	3.78
NIST DPM 1650 Residue	180	0.34	172.0	1.11
Diesel Soot #1	174	0.47	141.0	3.99
Diesel Soot #3	177	0.28	150.0	3.60
Diesel Soot #4	186	0.61	123.0	3.82
Diesel Soot #5	186	0.61	124.0	3.00

a) The frequency of the measurement was 100MHz; at this frequency the Q value of the empty coil is 258.

b) Residue is the insoluble part after 24 hrs extraction with dichloromethane in a Soxhlet extraction system.

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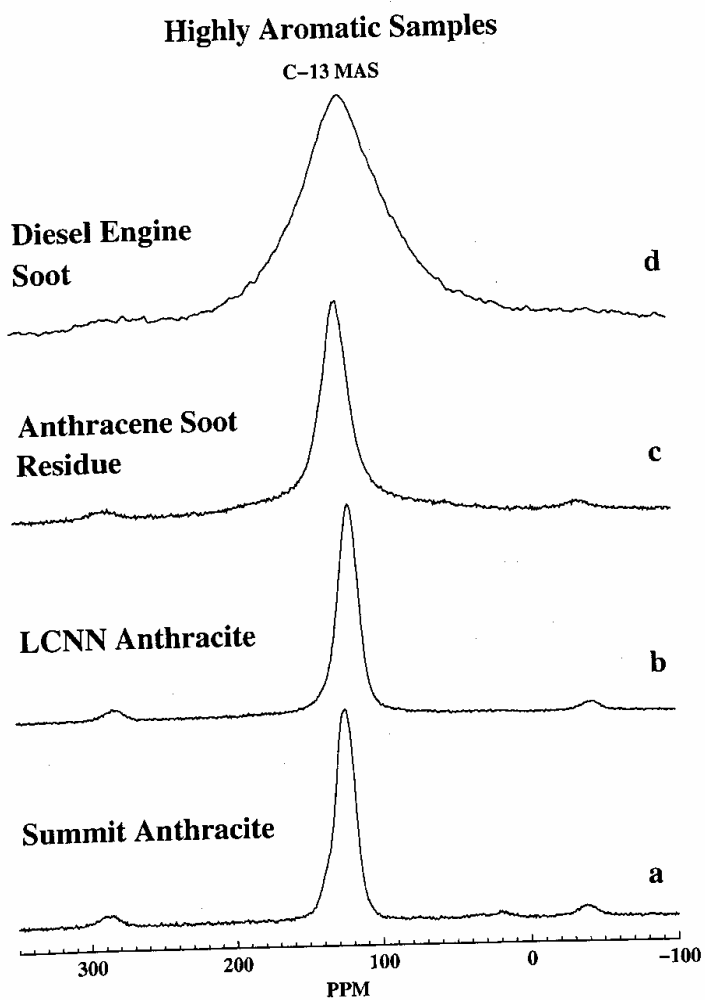


Figure 1. Carbon-13 MAS spectra of four of the samples. The spectra in a, b, c were taken with the CP technique all with a 1 s pulse delay. a) 3 ms contact time b) 10 ms contact time, c) 10 ms contact time d) spectrum taken with the single pulse method and using a 10 s pulse delay.

TEM studies of ultrafine PM from diesel and jet engine exhausts

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Introduction

There is considerable concern over the possible health effects of ultrafine PM, typically defined as PM $<0.1\mu\text{m}$ in mean diameter. Although such PM constitutes a relatively small percentage of the overall mass of PM_{2.5}, it accounts for a large percentage of the number of airborne PM_{2.5} particles, is easily inhalable into human airways, and presents a large surface area and very fine particle diameter to interact with and penetrate cell walls.

In the current study, transmission electron microscopy (TEM) has been used to investigate ultrafine carbonaceous PM derived from diesel and jet engine exhausts.

Experimental Procedure

Microscope:

The principal instrument used was a JEOL 2010F high resolution TEM. This microscope has a field emission gun, windowless EDX spectrometer, high angle dark field detector, peltier cooled 2048x2048 CCD camera for imaging, and a separate peltier cooled CCD camera for parallel EELS spectroscopy.

Sample Preparation:

Sample preparation for TEM observation is usually trivial but vitally important. We have used several sample preparation techniques. For large powder samples ($>200\text{ mg}$), a TEM grid is carefully immersed in the dry powder and twisted around. The grid is removed from the powder sample, tapped a few times to dislodge large, loose, agglomerates and observed in the TEM.

For smaller quantities of loose powder (a few mg), the powder is suspended in about 5 mL of acetone and ultra-sonicated for several hours. A few drops of the suspension are placed on the TEM grid and observed in the TEM. This technique consistently provides excellent TEM samples with a uniform distribution of particulates of controllable surface density. Though this has been the most widely used technique for sample preparation, it has an inherent problem that acetone soluble components can be leached out, altering the chemistry of the sample.

In-situ TEM sample preparation by collecting the sample directly on the grid is usually more difficult but yields the highest quality pristine samples. A TEM grid has to be able to withstand the physical conditions (temperature, flow, ambient cleanliness) of the sample collection point to collect samples in this manner.

Results and Discussion

Diesel PM:

Six samples of diesel PM were prepared in a two-cylinder diesel engine test facility at the University of Utah combustion laboratory. As discussed in other sections of this report, the samples were prepared from three different diesel fuels with the engine running under idle and load conditions. Although several other techniques were able to discern significant differences in graphitic content versus unburned diesel fuel and lube oil content for different fuels and running conditions, we were unable to detect clear differences between the various samples using TEM. This is undoubtedly because of the nature of the technique, which is capable of examining only a limited number of particles in detail and is not readily adaptable to discerning “whole sample” properties unless the sample is quite uniform in nature. Nevertheless, the high-resolution TEM (HRTEM) results provide considerable insight into the nature of the “graphitic” structure of the soot and the fractural nature of diesel PM.

The TEM samples were prepared by dry and acetone suspension methods. Typical TEM images at several magnifications are shown in Figures 1-3. Relatively low magnification images indicate soot particle agglomerates in which the primary diesel PM globules (20 to 50 nm in size) are contained in chain-like structures (Figure 1)

Due to the “kinks” in the structure, these soot particles have a tendency to physically interlock with each other to produce larger agglomerates. This physical interlocking is strong enough to survive sonication in acetone for over an hour. These structures are three-dimensional even at the nanometer scale. Since TEM can “see through” the particles, the images do not show this third dimension information, except that they become little less transparent when stacked over each other.

At higher magnifications, TEM reveals the internal structure of these primary diesel PM globules (Figure 2). Specifically, the globules show contrast due to graphene layers oriented such that the planes are parallel to the electron beam. Typically these graphene layers are contained in stacks of up to ~10 (002) planes with linear dimensions ~5-20 nm. These stacked graphene layers are not completely parallel and are predominantly curved, forming onion-like structures. The interplanar distance between the graphene layers is not fixed and varies from approximately 0.33 to 0.5 nm (the 002 spacing of graphite is 0.337 nm). There are number of “onions” in a single globule of a diesel soot particle varies from about 1 to 10, with some onions only 2-3 graphene layers thick.

Jet engine PM emissions:

PM samples from a jet engine exhaust were collected at the T-80 test combustion facilities of the Wright Patterson Air Force Research Laboratory in collaboration with Edwin Corporan and Bill Harrison of the AFRL and Matthew DeWitt of the University of Dayton Research Institute of the University of Dayton. PM samples were directly collected on TEM grids using a heated smoke trail probe. Samples were collected during test runs using standard JP8 jet fuel with and without the addition of 10 volume percent of Norpar, a high purity Fischer-Tropsch additive, at both idle and cruise conditions. Both SiO substrate and holey C substrate TEM grids were used for PM collection. Holey C substrate grids showed the presence of individual fine PM particles

uniformly dispersed over the entire area as well as some large aggregates of PM sparsely sprinkled over the grid. However, PM deposition on the SiO substrate appeared to have been strongly affected by the local airflow patterns. Total quantity of deposited PM was much smaller and there were no large aggregates of PM. Consequently, very little time was spent in analyzing the samples collected on SiO grids.

The holey C substrate showed many particles attached to the C substrate and hanging over the holes. These particles appeared to be growing out of the C substrate as there was no clear demarcation where the substrate ended and particles began. Some of the features appeared to be developed by condensation of the vapor phase to semi-liquid/solid phase right on the substrate.

TEM analyses of the jet PM samples with and without the Norpar additive did not reveal any major differences in the PM morphology and microstructure, even though the Norpar additives to the jet fuel caused significant reductions in PM emissions. However, there was a definite difference between PM samples collected under idle and under cruise conditions. The idle condition samples were more heterogeneous with larger amounts of non-carbonaceous matter than the cruise condition samples. The morphology of the fine PM in cruise samples showed structure rather similar to the structure of diesel PM, that is, chain-like structures of globules 20-100 nm in mean diameter (Figure 4). The morphology of the PM aggregates obtained under idle conditions showed larger agglomerated particles with knobby rough surfaces and almost no chain like growth (Figure 5).

It is also worth noting that the jet PM contains significant amounts of several inorganic elements. Results obtained by XRF analysis conducted by Prof. Dave Robertson are shown in the table below. Typical STEM x-ray maps of a PM particle containing Fe-rich metallic inclusions are shown in Figure 6.

XRF results of selected elements for jet PM (ng/cm²)

Sample Name	P	S	Ca	Fe	Co	Ni	Zn	Ga	Ba	Pb
Average of 3 Blanks	0	0	5193	227	12	5.5	38.1	0	1213	74
Filter 34 JP8 @idle	773	731	5995	555	48	53	143	6.7	1940	65
Filter 40 JP8 @cruise	939	112	6022	377	0	24	80.8	0	1600	60
Filter 42 JP8+Norpar @idle	362	63	5875	344	19	7.4	125	4.5	1930	81
Filter 45 JP8+Norpar @cruise	377	95	6354	405	6.7	22	131	5.9	1840	72

A major problems in TEM analyses of the jet PM samples was the electron beam damage to the sample. Apparently, the jet PM sample contained enough volatile organic material to heat up, volatilize, interact with the beam and re-deposit back on the sample to create unusual and misleading artifacts. This phenomenon usually got more severe with higher energy density of

the beam at higher magnifications. Typical structures formed are shown in Figure 7. Because of this unusual problem, we could not analyze the samples at high enough magnifications to detect any graphene layers or onion structures. Drying the sample overnight under an infrared lamp (~60-80 C) overnight did not alleviate this problem. We will attempt solvent extraction to alleviate this problem in the near future.

Summary and Conclusions

High resolution TEM provides significant insight into the structure of carbonaceous PM emitted from diesel engines. Two significant observations should be emphasized.

2. Diesel PM exhibits a distinctive microstructure that consists primarily of three dimensional chain-like structures of 20-100 nm primary PM globules.
3. High magnification, high resolution TEM reveals that the primary globules consist of onion-like structures made up of graphene layers. Typically 3-10 graphene layers make up the “onion rings”, with the layer spacing decreasing from approximately 4.5 to 3.4 nm as the number of layers increases.

TEM has also been used to examine PM derived from a jet engine. The jet PM samples were collected in collaboration with Edwin Corporan and William Harrison of the Air Force Research Laboratory (AFRL) at the Wright Patterson Air Force Base and Matthew DeWitt of the University of Dayton Research Institute. The preliminary results are as follows.

1. With the jet engine running under cruise conditions, chain-like structures of 20-100 nm primary PM globules very similar to the diesel PM are observed. Under idle conditions, however, larger more equant agglomerates are observed.
2. Attempts to observe graphitic structures at higher magnification were unsuccessful, due to the growth of unusual fibrous carbon structures. Such structures could arise from the volatilization and re-deposition of unburned fuel and lube oil.

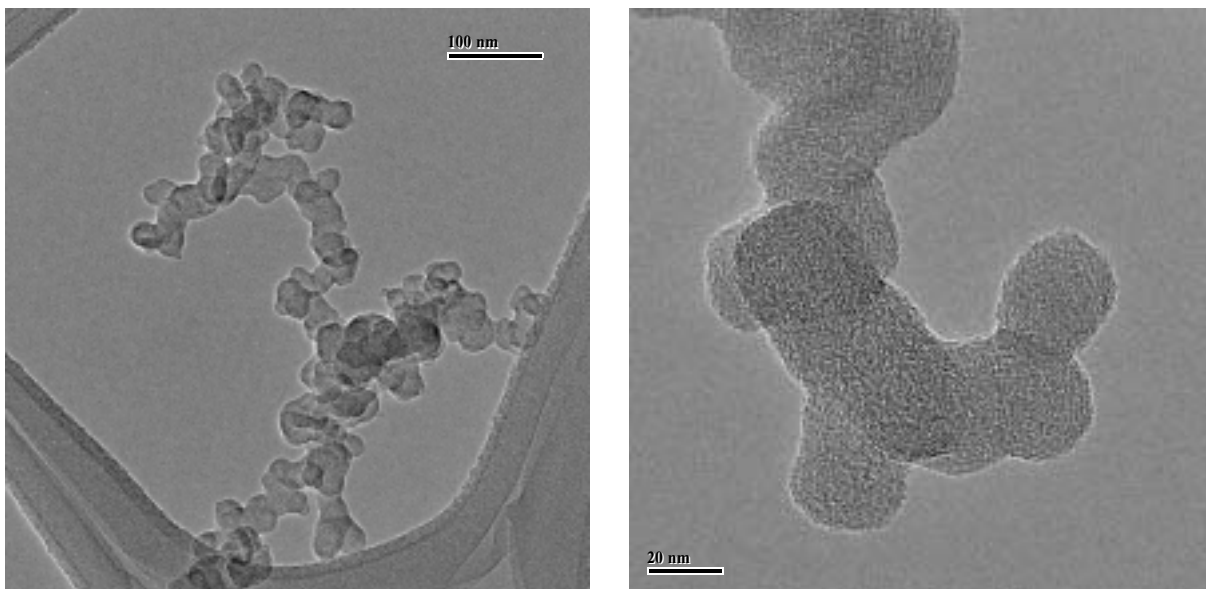


Figure 1. Chain-like agglomerates of primary diesel PM particulates.

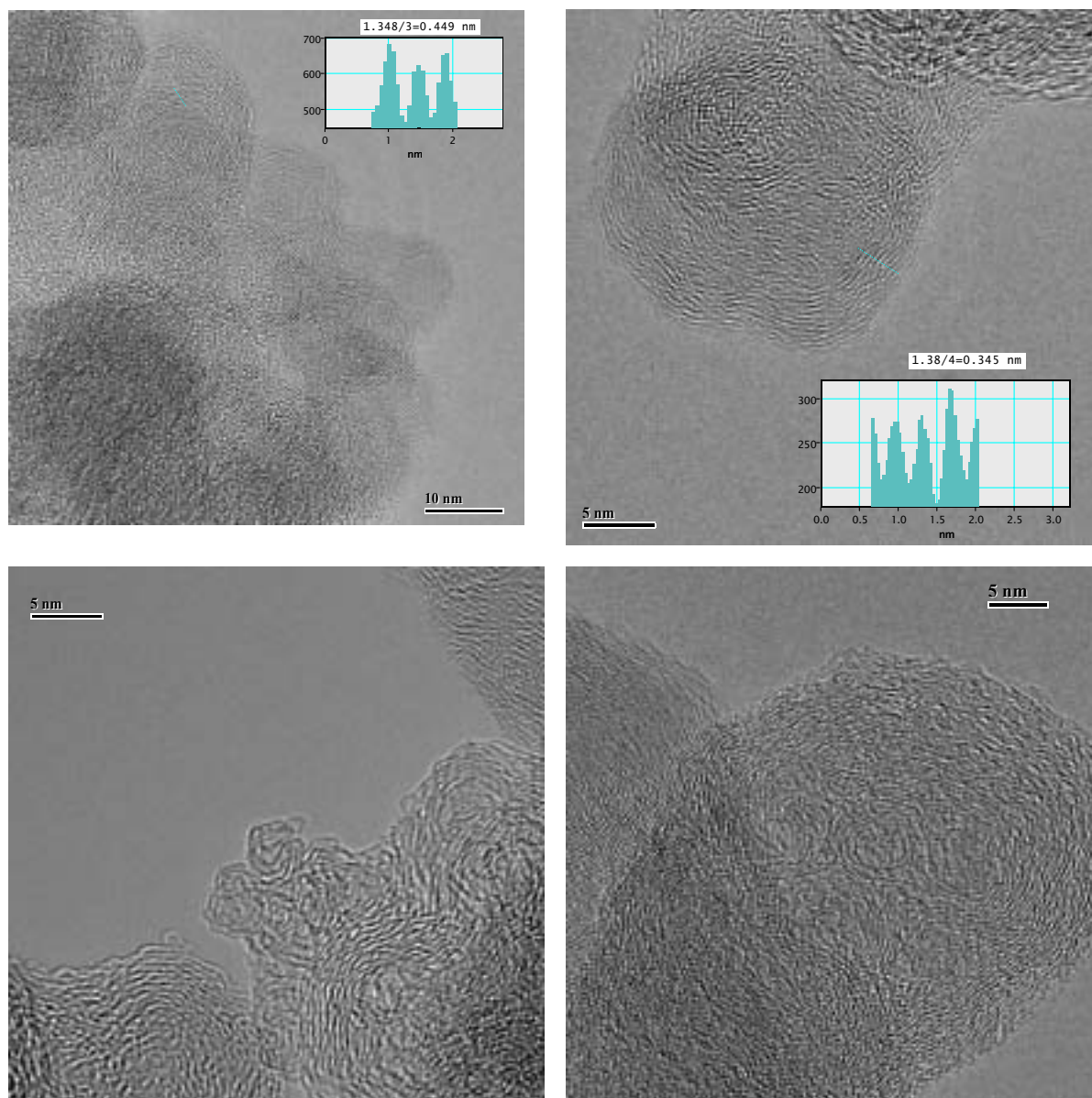


Figure 2. HRTEM micrographs showing the nature of the nanoscale graphitic regions in diesel particulates. The onion-like graphene layer structures are quite distinctive.

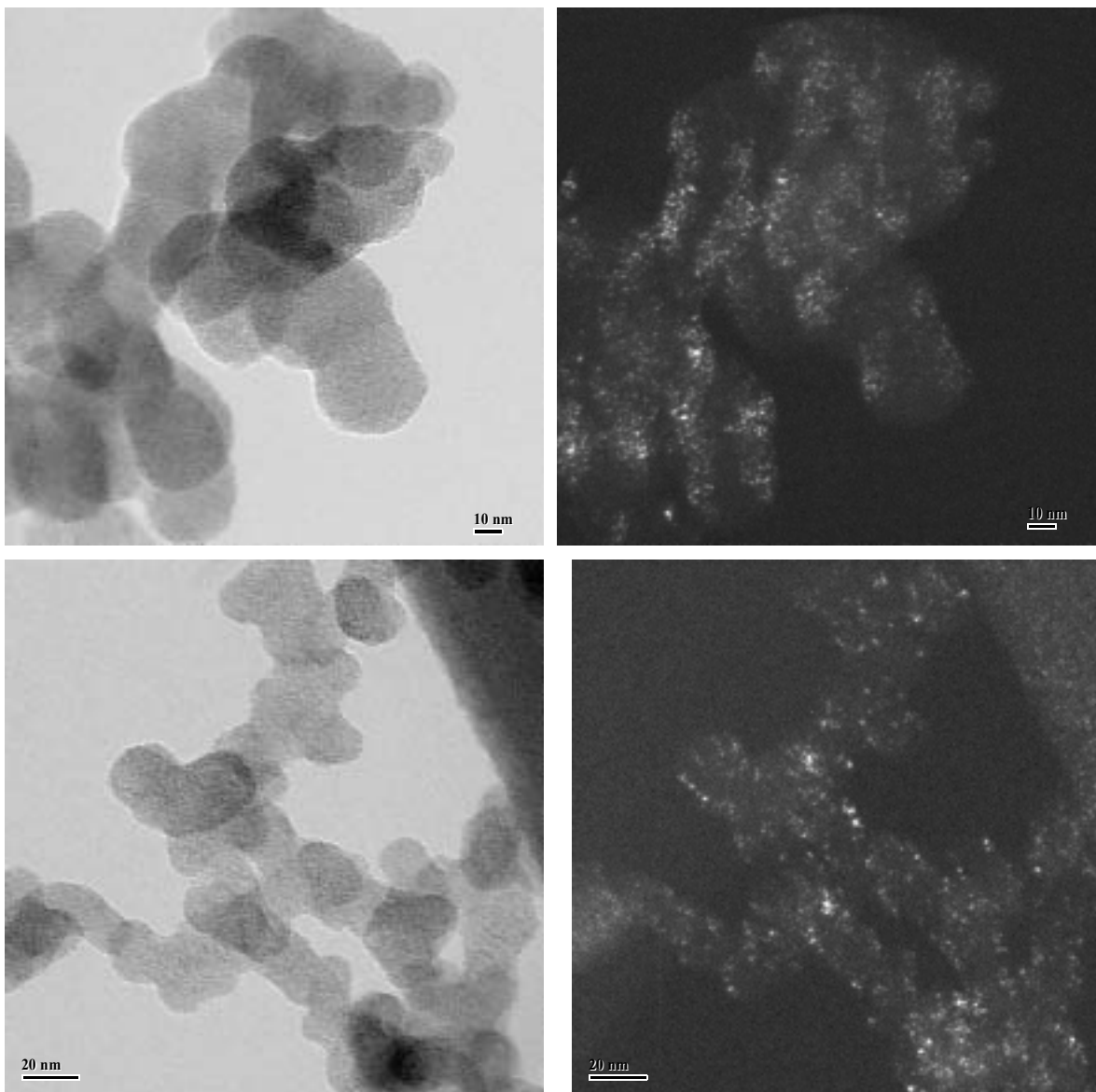


Figure 3. (000) bright field and (002) dark field images of soot particles containing several primary globules. Note that the bright areas in the dark field images, which are due to regions meeting the 002 Bragg condition.

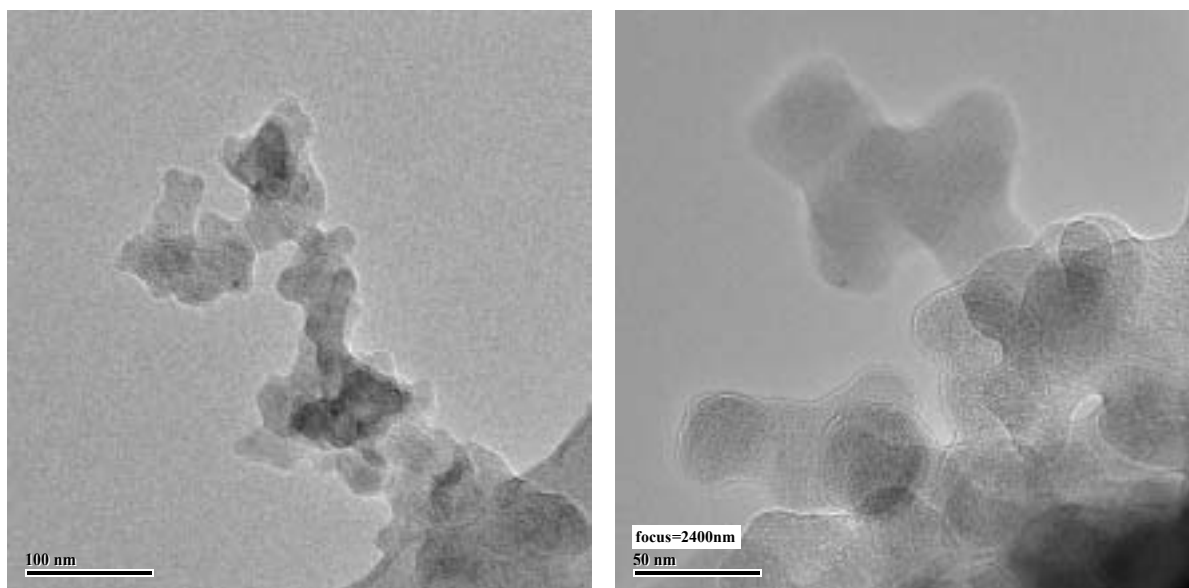


Figure 4. Chain-like structures of 20-100 nm globules observed in PM from a jet engine running under cruise conditions are similar to those observed in diesel engine PM.

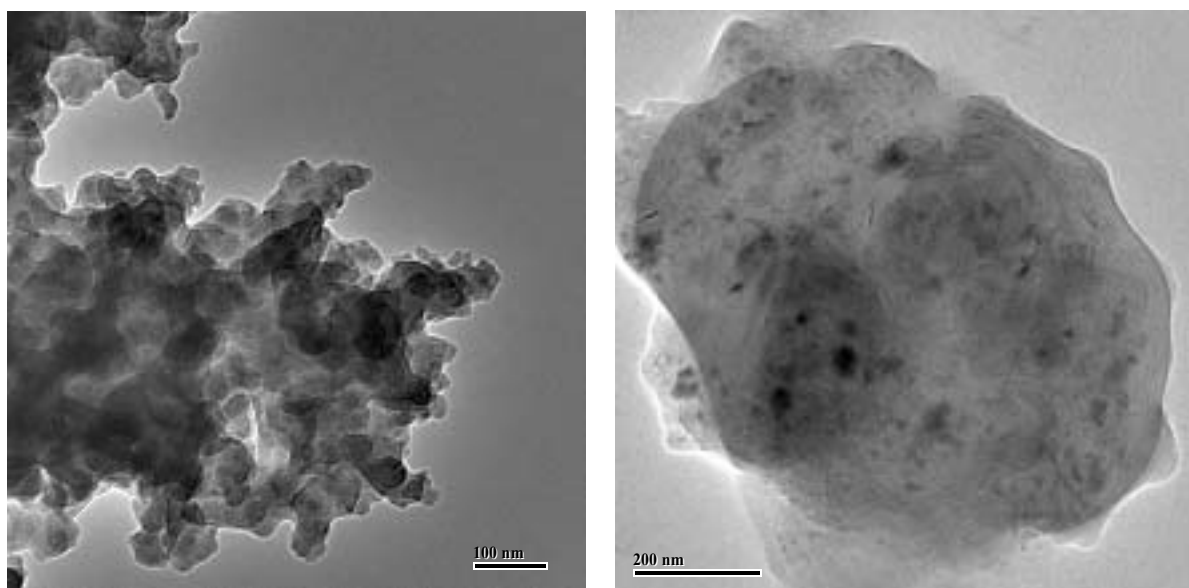


Figure 5. Jet PM collected under engine idle conditions tends to consist of larger, more condensed aggregates. Inorganic inclusions are evident in the particle on the right.

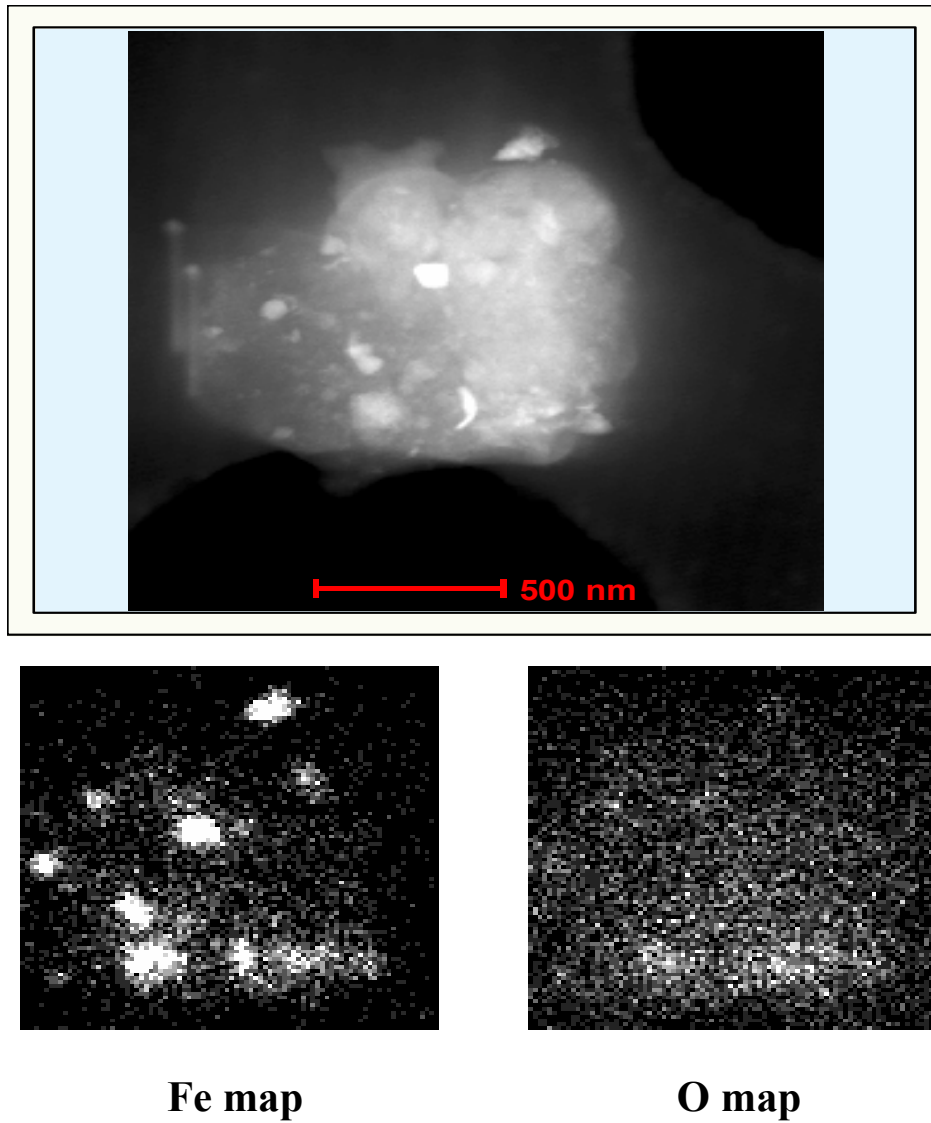


Figure 6. This stem image and Fe and O x-ray maps of a jet PM particle show that it contains nanoscale Fe-rich particles that are predominantly metallic.

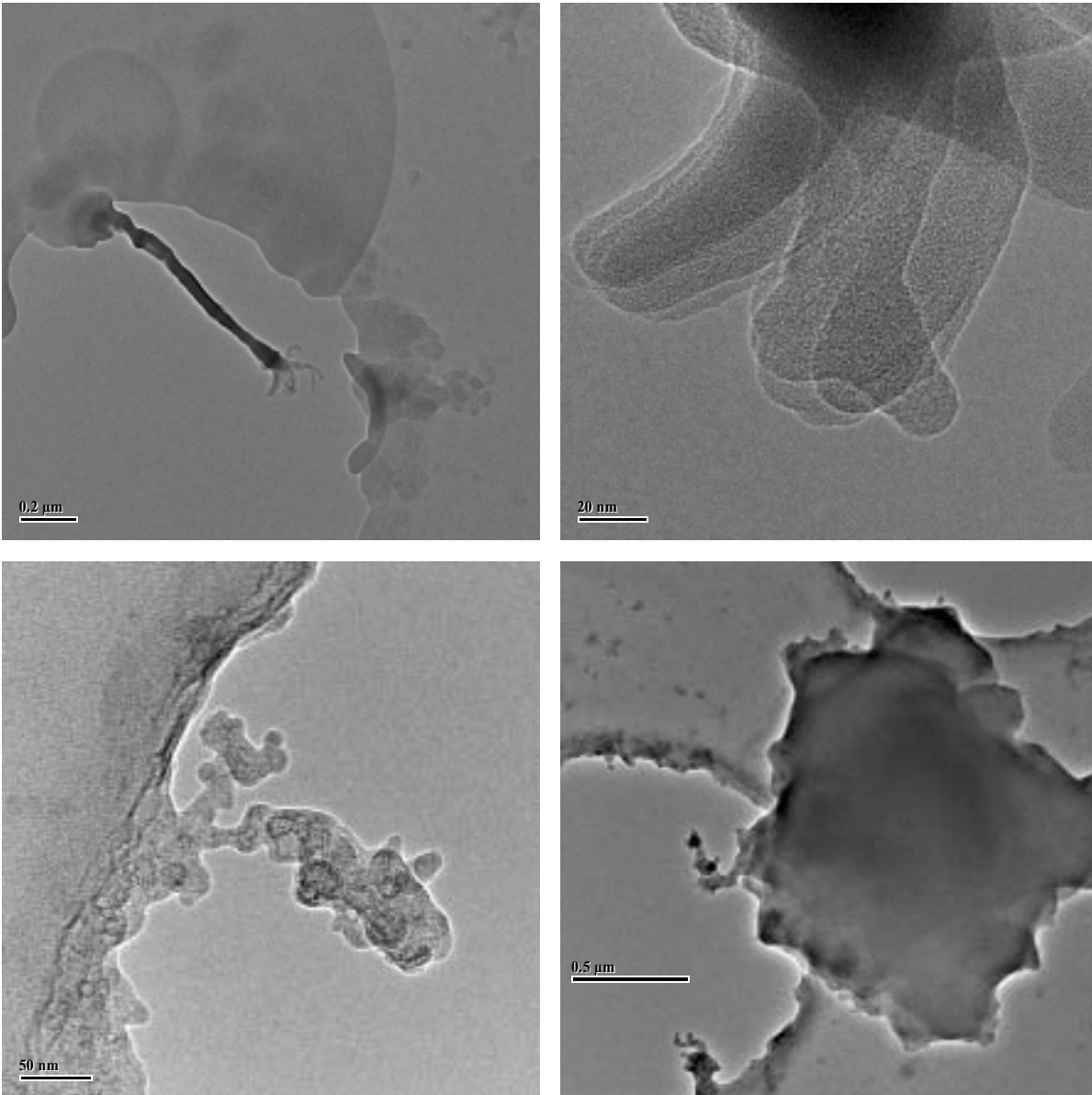


Figure 7. TEM micrographs illustrating unusual fibrous carbon structures produced when attempting to investigate the jet PM under high resolution, high magnification conditions.

Gas Chromatography/Mass Spectrometry and Multivariate Data Analysis of Organic Combustion Signatures in Ambient Particulate Matter

Henk Meuzelaar, Neil Arnold, SueAnne Sheya and JoAnn Lighty

Research activities during the past year have focused on: (1) deconvolution and identification of organic combustion signatures in complex urban PM samples; and (2) generation, collection and characterization of diesel engine soot samples under well-defined operating conditions.

I - Combustion Signatures in Ambient PM Samples

Thermal Desorption (TD) GC/MS profiles from 24-hr ambient PM samples, collected on quartz fiber (QF) filters at 11 different receptor sites within the Paso del Norte airshed along the US/Mexico border, were examined for organic combustion signatures using exploratory factor analysis techniques.

The Paso del Norte airshed encompasses the sprawling megacity of Juarez (pop. ~ 1,800,000) and the city of El Paso (pop. ~ 200,000) separated only by the Rio Grande River and accompanying border clearance zone. Due to marked contrasts in culture, economic development, industrial practices and environmental regulations, the large metropolitan area formed by these nearly contiguous cities is home to a highly complex assortment of ambient PM sources. Combustion-type PM sources range from a broad array of mobile sources and industrial furnaces to open kilns, ovens, piles, drums and pits burning all manner of biomass and waste products. In view of this extreme complexity, compilation of a comprehensive inventory of organic PM emission sources, particularly on the Juarez side, is virtually impossible.

Therefore, we used detailed speciation of organic PM components in spatially distributed receptor samples by TD- GC/MS in combination with exploratory Factor Analysis in order to numerically extract prominent organic combustion signatures while trying to reference these to known geographical concentrations of certain types of combustion sources. As reported by Sheya [1], this approach has enabled us to recognize specific biomass combustion sources, including fireplaces and brick kilns, as well as urban dust sources and mobile sources.

Figure 1A reveals a spontaneous demarkation between factor analysis scores produced by TD-GC/MS profiles of PM-associated organics in 11 receptor samples obtained on different sides of the US/Mexico border. The corresponding factor loading plot in fig. 1b demonstrates this demarkation to be primarily due to higher relative concentrations of polynuclear aromatic hydrocarbons (e.g. associated with brick kilns and other soot-forming combustion processes) plus animal fatty acids (primarily associated with cooking) on the Mexican side of the border and of fossil terpenoids (associated with incomplete combustion of petroleum-derived fuels) plus alcohols and ketones (e.g., associated with automotive catalytic converters) on the US side. The chemical process associations used here are largely based on the pioneering work of Cass et al. [2]. The results of rapid, exploratory source attribution studies such as this allows one to zoom in on key PM-associated compound suites representative of certain classes of combustion sources, thereby reducing the problem of myriads of different individual combustion sources in the Paso del Norte air basin to more manageable proportions. Furthermore, this approach

provides an important shortcut to population exposure risk studies, such as demonstrated by Mejia et al [3].

Notwithstanding the current emphasis on PM_{2.5} or PM_{1.0}, conventional PM₁₀ samples remain the logical choice for many broad-based scientific studies. Ambient particulate matter classifications such as "PM₁₀", "PM_{2.5}" and "PM_{1.0}" represent operational concepts whose primary relevance lies in a hypothetical mechanistic relationship, or empirically observed correlation, with possible health end effects. Use of these classifications outside their narrow operational boundaries, e.g., in order to try and answer fundamental scientific questions about PM formation and distribution mechanisms, is likely to result in artificially skewed measurement data. Moreover, exclusion of organic chemical combustion signatures associated with larger ambient particles, e.g., in the 3 - 7 micron range, violates two fundamental principles of multivariate statistical analysis, namely: (a) to strive towards a multivariate normal distribution of measurement data; and (b) to avoid a-priori data exclusions, whenever practical. Fortuitously, inclusion of a broader range of particle sizes does not at all preclude the possibility of investigating the potential relationships between particle size and particle composition. As long as the intrinsic dimensionality of the measurement data space is large enough to accommodate the major sources of variance associated with particle size it may prove possible to numerically extract the various signatures involved. In fact, as demonstrated by Windig et al [4] numerical deconvolution of spectroscopic signatures in complex organic matter is often possible, even in the absence of known instrumental separation methods.

II - Collection of Well-defined Diesel Soot Samples

PM source modeling calculations, based on emission inventories in combination with known emission factor and PM dispersion/deposition behavior assumptions, indicate that in urban air sheds where diesel engines constitute more than a few percent of all mobile sources, diesel soot tends to become the dominant source of ambient carbonaceous PM, particularly in the fine particulate matter range [5]. Thus far, there appear to be no reliable analytical methods to distinguish individual diesel soot particles from other soot producing sources. Nonetheless, the work of Cass et al. [2] on has produced sufficiently characteristic combustion signatures for PM-associated organic compounds to enable source apportionment which distinguishes between diesel and gasoline engines as well as between automotive engines with or without catalytic converters. Since recent reports suggest that: (a) ambient soot-type PM may have a disproportionately large negative effect on morbidity and mortality [6]; and (b) atmospheric soot-type PM could have a marked effect on global warming and cooling [7], it would seem to be quite important to develop a more rational chemical classification of diesel soot components than achievable by the current, archaic "organic carbon" vs. "black carbon" classification techniques.

As argued in a recent editorial [8], similar procedure-dependent operational concepts such as "fixed carbon" in coal science or "humic acid" in soil science have only served to delay the introduction of more rigorous analytical methodologies and chemical classifications in these research communities. Moreover, terms such as "organic carbon", "black carbon", or "inorganic carbon" are in direct conflict with accepted scientific definitions of the terms "organic", "black" and "inorganic", respectively. In view of the above-described crucially important role of soot-type PM in environmental health studies as well as in physico-chemical atmospheric models a better founded scientific description and classification of carbon structures and forms in ambient particulate matter is urgently needed.

C13 NMR is one of the most powerful methods for characterizing highly condensed carbonaceous materials. Moreover, the empirical pyrolytic method currently used to determine the amount of "organic carbon" and "black carbon" in ambient PM samples neither meets reaction control criteria for modern "analytical pyrolysis" methods, nor uses advanced analytical techniques to determine the nature and concentration of the volatile compounds evolved, e.g., such as described by Dworzanski et al. for char and soot-type materials [9] by means of TG/MS methods. However, in order to use both TG- and NMR-based analytical methods, it is desirable to collect several grams of diesel soot under sufficiently well-defined reaction conditions to enable a meaningful comparison of carbonaceous structures and compositions. To this end a small diesel engine test bed was developed, as described in previous reports [10]. However, preliminary analysis of the PM samples obtained by TD-GC/MS (Dr. Meuzelaar & co-workers), C13NMR (Dr. Pugmire & co-workers) and XRF (Dr. Robertson & co-workers) techniques suggested that conventional hi-vol QF filter sampling, using well-defined filter flows, produces unacceptably large variations in the composition of PM collected on the QF filters because of filter temperature fluctuations caused by differences in diesel engine load and rpm.

This has prompted a complete redesign of the PM and VOC sampling train in collaboration with Dr. Sarofim and his associates David Wagner and Kerry Kelly. This redesign was completed in October 2002. Presently, a series of engine tests is being carried out which aims to produce gram quantities of diesel engine soot samples from well-characterized diesel fuels, fuel blends and additives under well-defined engine operating conditions. These samples will be made available to Dr. Pugmire's group for C13 NMR analysis and will further be investigated by conventional "organic carbon vs. black carbon" test procedures as well as the more advanced analytical pyrolysis methods discussed previously. Also, in close collaboration with Dr. Sarofim & associates we will be attempting to determine the effect of variations in engine exhaust temperature and residence time on soot composition. The results of the various analytical methodologies will be integrated and compared by means of canonical correlation methods for multisource analytical data, such as reported by Meuzelaar et al. [11].

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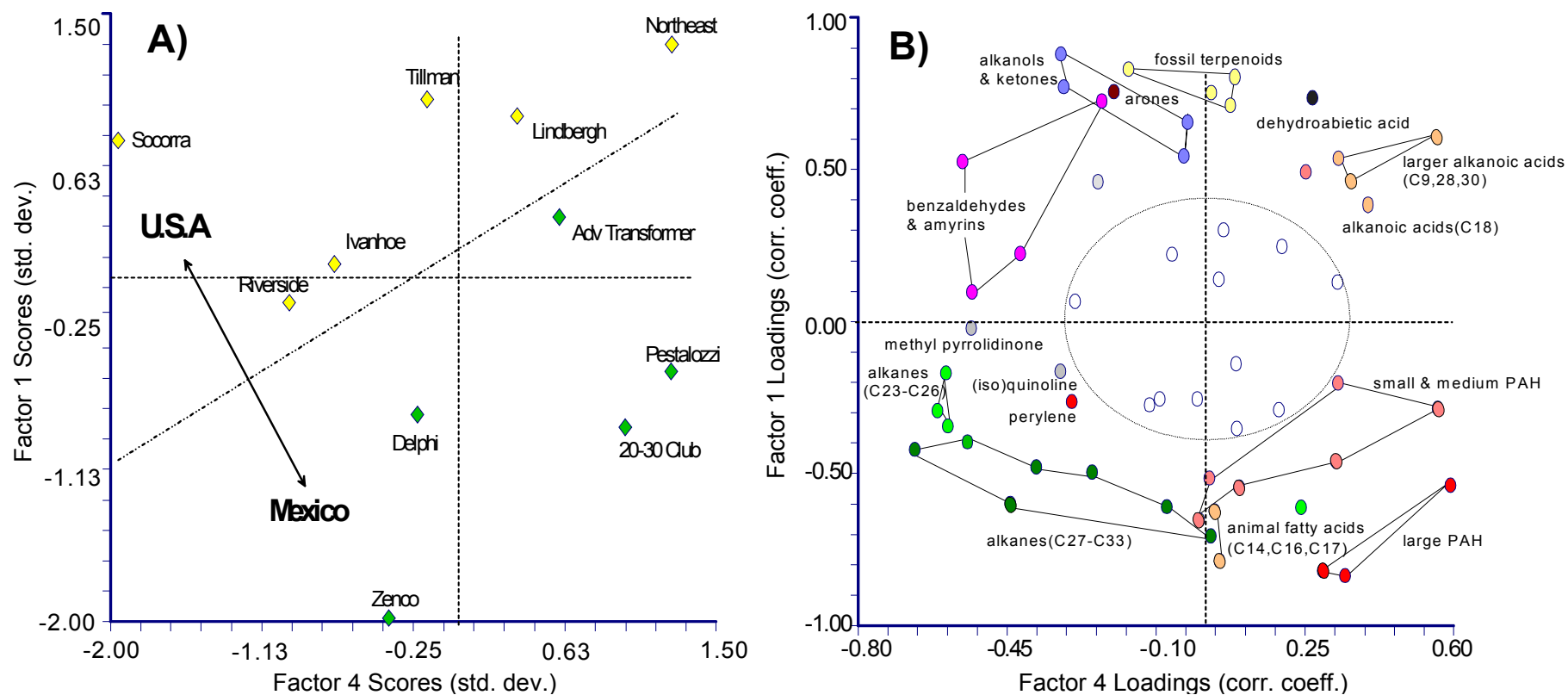


Figure 1. Factor 1 versus factor 4 scores A) and loadings B) for TD-GC/MS profiles of PM10 receptor samples from 11 Paso del Norte sites. The US sites can be separated from the five Mexican sites in these plots which represent 27% of the total variance.

Generation and Analysis of Particulate Matter Emissions from Combustion Sources

A.F. Sarofim and J.S. Lighty, University of Utah

Generation of Well-Defined Diesel Soot Samples

Because diesel PM is such an important contributor to fine PM concentrations in the atmosphere and diesel PM composition can vary dramatically with fuel and engine condition, the investigators have been upgrading their diesel engine test facility to provide more consistent and reproducible conditions. The upgrades focused on improving engine control, temperature sensing, air-flow monitoring, and fuel consumption. With the upgrades, an operator can monitor and record a number of parameters, such as brake-specific fuel consumption and horsepower (Figure 1).



Figure 1. Example of the parameters that are now monitored in the engine test facility.

The two-cylinder, 482 cc Kubota diesel engine was upgraded with improved sensing and control elements to monitor and control engine conditions. Specifically, an auto throttle servo and an auto load servo valve improved engine control. Both provide feedback to a software system that controls engine rpm and engine load, as provided by a water-brake, direct-shaft mounted dynamometer. A data channel expansion unit was installed to automate the throttle and load control. This enables the operator to view and adjust engine speed and load, and also accommodates preprogrammed transient cycles.

In order to ensure reproducible test conditions, the engine was also upgraded with a number of sensors. Engine oil and coolant temperatures are monitored with thermistors;

intake, exhaust manifold, and critical sampling points are monitored for temperatures with thermocouples. In addition, incorporating a cold-junction compensator enhanced the accuracy of the temperature measurements.

Air flow meter turbine units were installed to measure exhaust and intake rates. The exhaust can now be quantified by adjusting the exhaust gas density in the interface software or by initial calibration using the Kubota engine manufacturer's performance data. The intake air now passes a series of high surface area HEPA filters prior to the intake air flow meter turbine. Using the HEPA-filtered intake can help determine the effect of PM in the intake on the formation of PM in the exhaust.

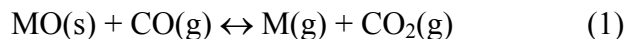
Fuel consumption is now automatically measured with a low-volume flow sensor that reports fuel consumption to the software interface. For very low fuel consumption rates, a digital laboratory bench scale with real-time updating can be used. This requires that an external fuel tank be placed on the scale, and the scale is equipped with RS-232 output, which reports mass to a computer.

Diesel Engine Experimental Plan

With completion of the engine upgrades, the investigators have developed a set of experiments to determine the effect on PM of engine operation conditions and fuel composition. The current test matrix involves varying engine load, cetane number, composition (fixed cetane number), and composition (variable cetane number). Currently, it comprises forty different tests, and it may be revised as the tests progress. Each set of tests will be performed at three conditions: 1200 rpm (idle), 1600 rpm with 10 ft-lb torque, and 2500 rpm with 10 ft-lb torque.

The Role of CO₂ in the Vaporization of Metal Oxides from Coal Combustion

Understanding the formation of submicron ash will become increasingly important as EPA begins setting standard limitations for the emission of hazardous air pollutants. The vaporization of minerals is proportional to the vapor pressure of CO and increases with increasing temperature. Vaporization of refractory oxides also increases in reducing atmospheres where a more volatile reduced species is formed via the reaction:

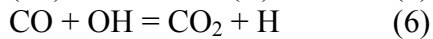
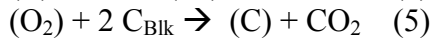
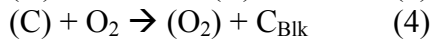
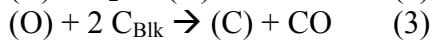
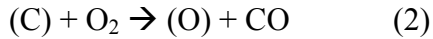


where M is a metal such as Fe, Mg, or Ca. Hence, the vaporization of refractory oxides may be suppressed by an increased CO₂ vapor pressure if the reverse reaction is important.

Since M has a higher vapor pressure than MO, the rate of vaporization will depend on the vapor pressure of M which in turn will depend on the CO₂/CO ratio and the

temperature. Increasing the CO₂ concentration will decrease the rate of vaporization. Inasmuch as the ambient CO₂ concentration surrounding burning coal particles can vary from near zero in laboratory experiments to tens of atmospheres in gasifiers, it is important to quantify the effect. The present program provides complementary theoretical and experimental programs aimed at developing a validated model for the vaporization of mineral constituents in coal.

At high temperatures the reaction given by Eq. 1 approaches equilibrium. The partial pressures of CO and CO₂ are controlled by a number of reactions. The reaction of O₂ with carbon gives a mixture of CO and CO₂, with CO dominating at high temperatures. The ratio of the CO₂/CO can be calculated as a function of reactions of carbon oxide complexes. An additional heterogeneous reaction involving the ratio is that of CO₂ with carbon to yield CO. The problem is further complicated by the gas phase reactions of CO with OH to form CO₂. These reactions are either highly endothermic or exothermic so that the reactions may influence the particle temperature. A model to represent both the gas and solid phase reactions has been developed by Prof. Haynes from the University of Sydney, Australia to simulate the heterogeneous reactions, the homogeneous reactions, diffusion in the porous chars, and the corresponding energy equations. The model approximates the surface reactions with the following subset:



The elements or compounds in paranthesis represent chemisorbed species, C_{Blk} represents the carbonaceous substrate, and the remaining are gas phase species. Reaction 6 is reversible and represents the gas phase conversion of CO to CO₂. An additional 21 gas phase reactions are added for the H₂/O₂ reactions governing the free radical concentrations of OH and H needed by reaction 6. The coupled reactions are solved for the concentration distributions in a coal particle and in the surrounding boundary layer. These reactions are solved together with Reaction 1 to obtain the vaporization rate of the mineral inclusions in coal. Some representative results are provided in Figs. 2, 3, and 4 for the case of silica vaporization. Fig. 2. provides the effect on the vapor pressure profiles for a 100 micron diameter particle and its boundary layer burning in three mixtures: 20 percent oxygen, 80 percent nitrogen; 20 percent oxygen, 25 percent CO₂, 55% N₂; and 20 percent oxygen, 78 percent CO₂. These results were obtained with a C/CO₂ rate constant of . This is a high rate and gives an upper bound for the reaction. As a lower bound the calculations were rerun with the C/CO₂ rate constant set to zero. The results are shown in Fig. 3.

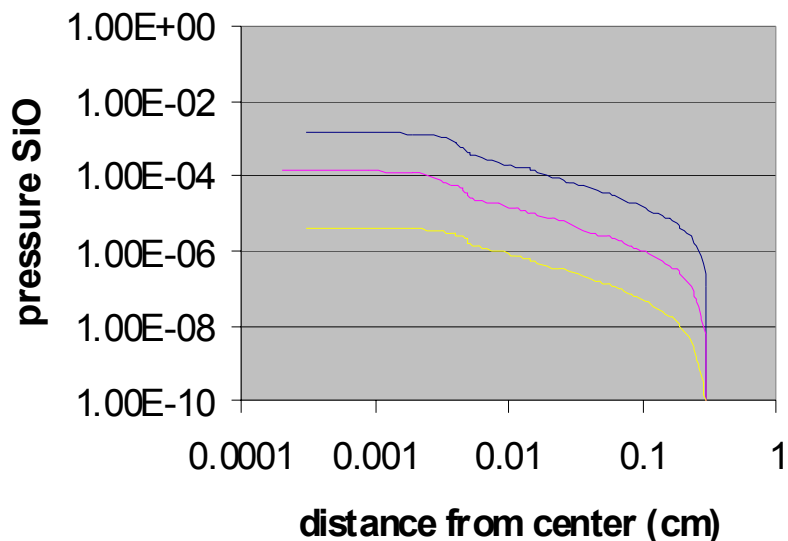


Fig. 2. The effect of changing the CO_2 concentration in the ambient gas on the calculated SiO radial profile. 100 micron diameter particle. Ambient temperature = 1700 K. Top curve: 20% O_2 /80% N_2 ; middle curve 20% O_2 /25% CO_2 /55% N_2 ; bottom curve 20% O_2 /80% CO_2 . Upper limit for CO_2/C reaction rate.

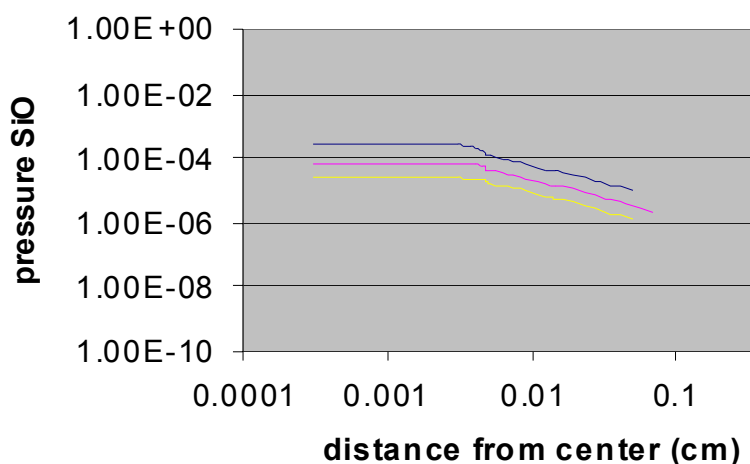


Figure 3. The effect of changing the CO_2 concentration in the ambient gas on the calculated SiO radial profile. 100 micron diameter particle. Ambient temperature = 1700 K. Top curve: 20% O_2 /80% N_2 ; middle curve 20% O_2 /25% CO_2 /55% N_2 ; bottom curve 20% O_2 /80% CO_2 . CO_2/C reaction rate = 0.

For the high CO_2/C reaction rate a close to three order of magnitude impact of CO_2/C reaction on the vapor pressure of SiO and hence on the SiO vaporization rate. The major reason for the large increase seen in Fig. A is that increasing CO_2/C reaction decreased the particle temperature significantly (see Fig. C). With the CO_2/C reaction turned off the predicted effect is much smaller.

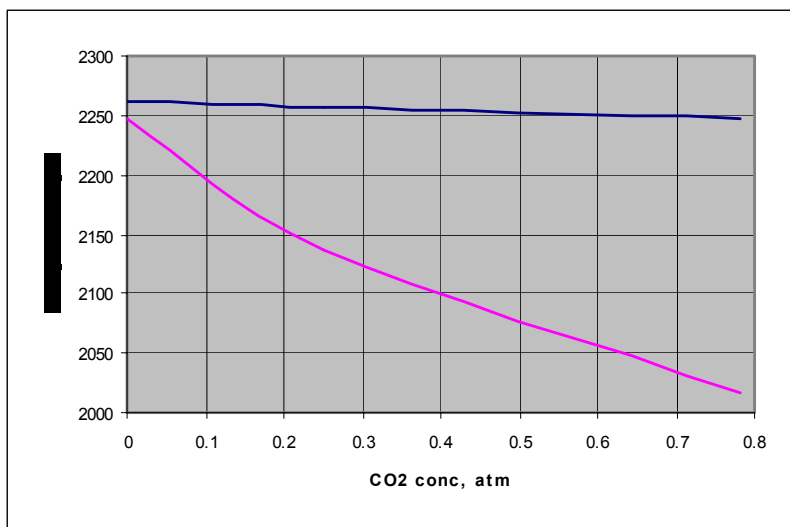


Fig. 4. The effect of CO₂ concentration on the temperature of a 100 diameter char particles, burning in mixtures of 20%O₂ with a balance of CO₂/N₂. Bottom curve for maximum CO₂/C rate, top curve CO₂/C reaction turned off.

The theoretical results showed that increasing CO₂ decreased the vaporization of refractory oxides such as SiO₂ by amounts that depend on the rate of the CO₂/C reactivity. Since literature values of the reactivity vary widely, experiments were conducted to guide the selection of rates that would predict the vaporization of the coals of interest for power generation in the U.S. The investigators studied the effect of CO₂ on the concentration of metals found in the particulate exhaust emissions. Ohio coal was burned at 1650 K in the University of Utah's drop tube reactor (Figure 5). The oxygen concentration remained constant at 50%, while CO₂ varied between 50%, 30%, and 10%. Nitrogen provided the remainder of the combustion environment. The oxygen/carbon dioxide environment allowed study of the impact of carbon dioxide on the reduction of refractory oxide metals in the submicron ash (indication of suppressed vaporization).

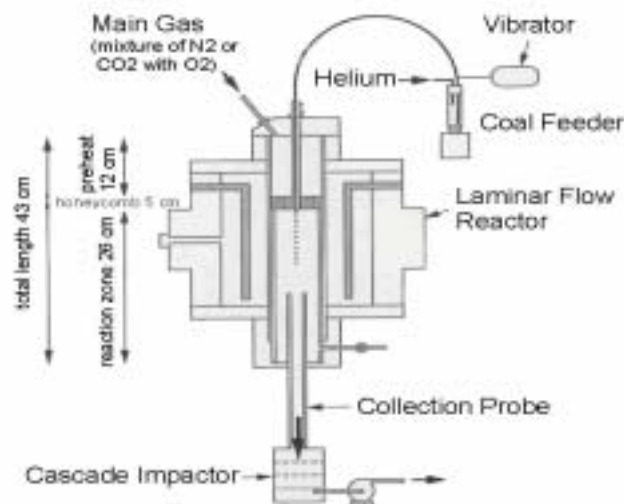


Figure 5. Drop tube reactor.

During the experiments, coal particles were fed to the furnace by pneumatic conveyance through a syringe feeding system at the rate of 1.2 g/hr. After combustion, the products rapidly cooled to 390 K with the addition of nitrogen gas and passage through a water-cooled probe. A MSP Corp. MicroOrifice Uniform Deposit Impactor (MOUDI), located directly below the furnace, collected size-segregated PM samples. The vertical arrangement allowed for collection of all combustion products. All stages of the MOUDI contained Durapore Millipore filters coated with Apiezon H grease, except the final filter which was ungreased. The grease prevented particle bounce from one stage to another. After a run, the MOUDI afterfilter, representing the submicron ash, was analyzed using X-ray fluorescence (XRF) by CRAEMS team member Prof. Robertson at the University of Missouri.

Carbon dioxide effects were seen on some metal vaporization, as expected. Quann found that the temperature in the drop tube furnace was unchanged when nitrogen was substituted by carbon dioxide [1]. This result is consistent with the zero value of the CO_2/C reaction in Fig. 4. Figure 6 illustrates the results of the experiments for total mass of coal vaporized. As shown in this figure, the vaporization of coal decreases with an increase in CO_2 concentration. As stated, the results shown in this figure, and the subsequent ones, are most likely a result of the change in gas environment and not temperature.

Figure 7 illustrates the effect of carbon dioxide on the vaporization of the major refractory oxides. The values shown are the ratios of the concentration at a given percent CO_2 condition to the concentration of that same metal at the 10% CO_2 condition. For these compounds, increased CO_2 concentration appeared to suppress metal

vaporization. This result is not surprising because silica, calcium, aluminum, and manganese are likely to form oxides versus other forms and exhibit the CO₂ effect.

The CO₂ effect was not evident in the concentrations of potassium, lead, and magnesium (Figure 8). Potassium should not exhibit the CO₂ effect. The results for sodium, chromium, and iron are inconclusive (Figure 9), and the investigators are currently examining the mineralogy of the coal in order to guide further experiments and identify potential reaction mechanisms.

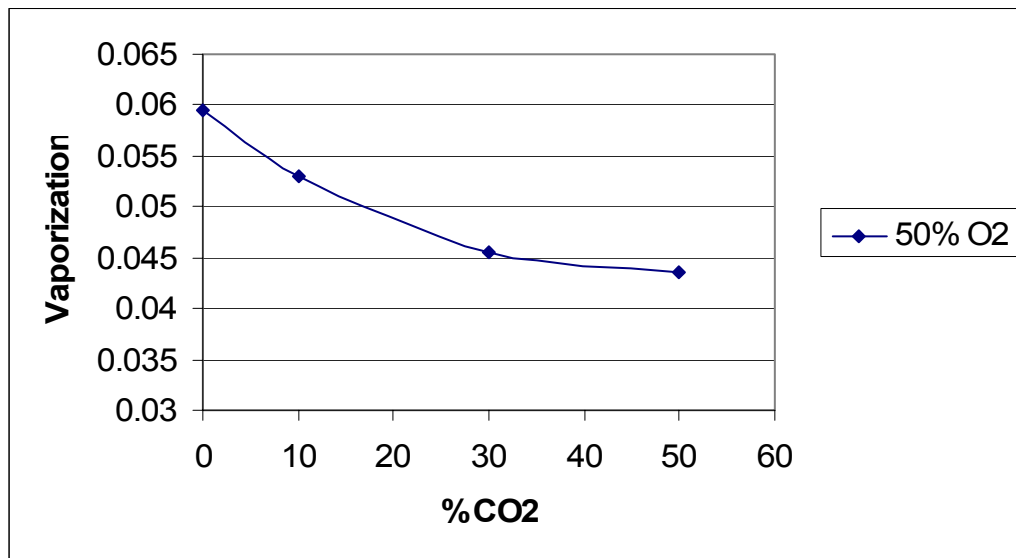


Figure 6. The effect of Carbon Dioxide on Mass Vaporized. Mass vaporized is determined by the mass on the final two filters divided by the mass of ash fed (coal fed multiplied by the percentage of ash).

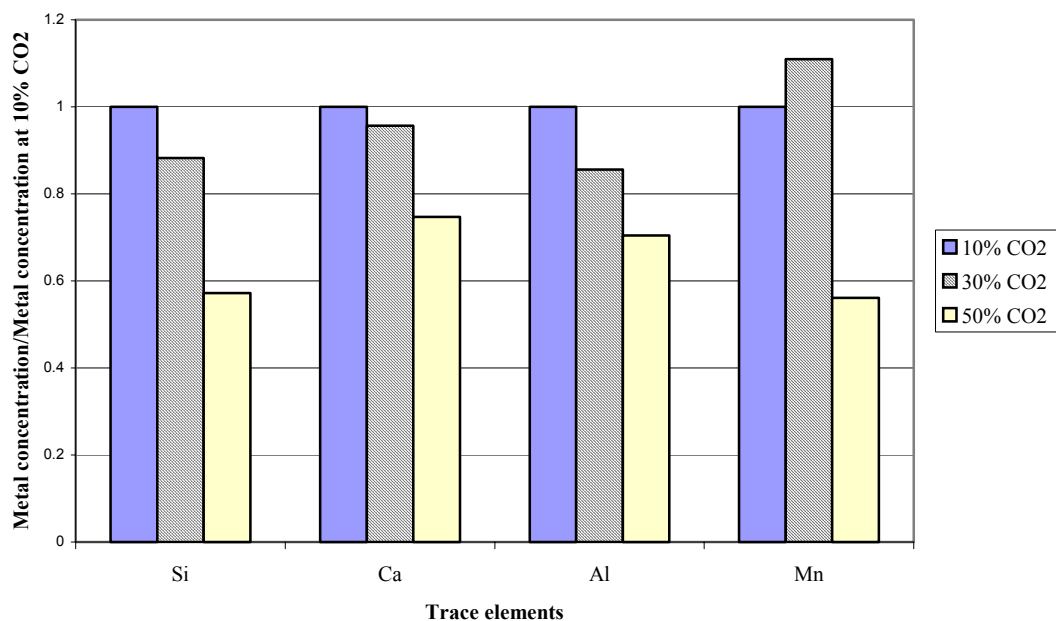


Figure 7. Effect of CO₂ concentration on the vaporization of silica, calcium, aluminum, and manganese.

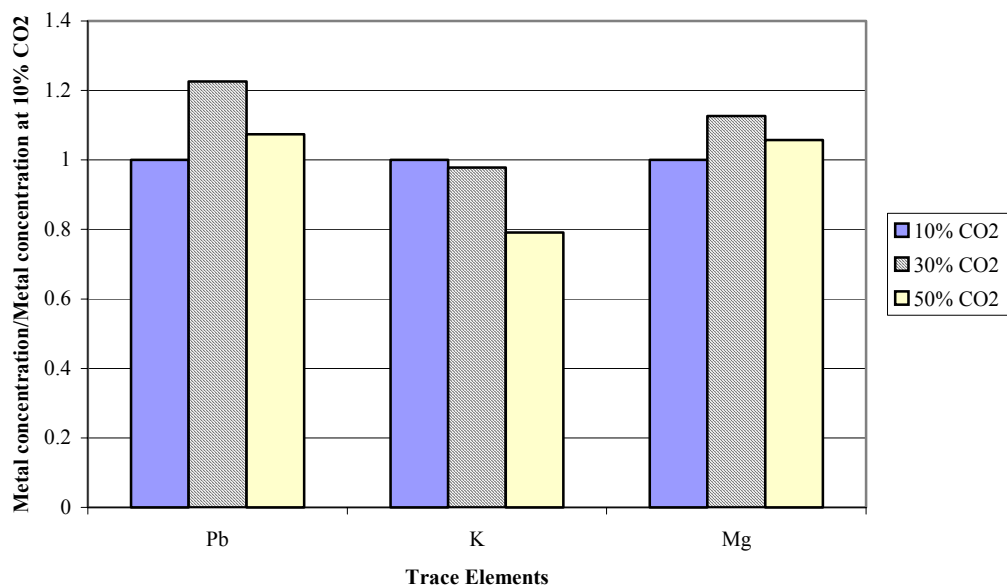


Figure 8. Effect of CO₂ concentration on the vaporization of lead, potassium, and magnesium.

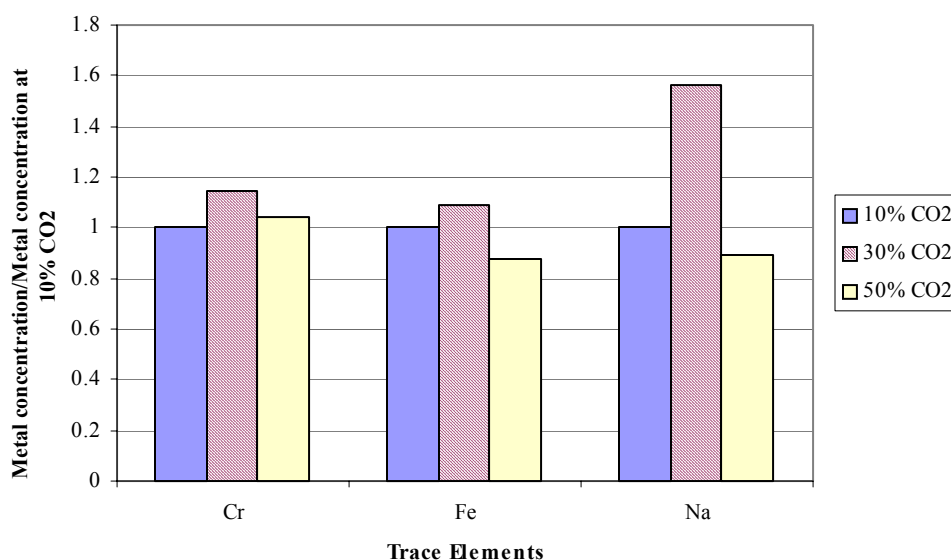


Figure 9. Effect of CO₂ concentration on the vaporization of chromium, iron, and sodium.

Effect of Biomass Co-firing on Coal Combustion

The investigators performed a preliminary study to examine the effect of co-firing biomass on coal combustion. The University of Utah's 5 million BTU/hr combustor fired natural gas, Utah coal, and mixtures of natural gas and biomass. The samples were collected in the transition zone, before the heat exchanger. A cyclone removed the largest particles, and a MicroOrifice Uniform Deposit Impactor collected size-segregated PM samples. In addition to the impactor samples, particle size distributions were also determined (Figure 10) with the scanning mobility particle sizer. The impactor samples will be sent to the CRAEMs collaborators for analysis.

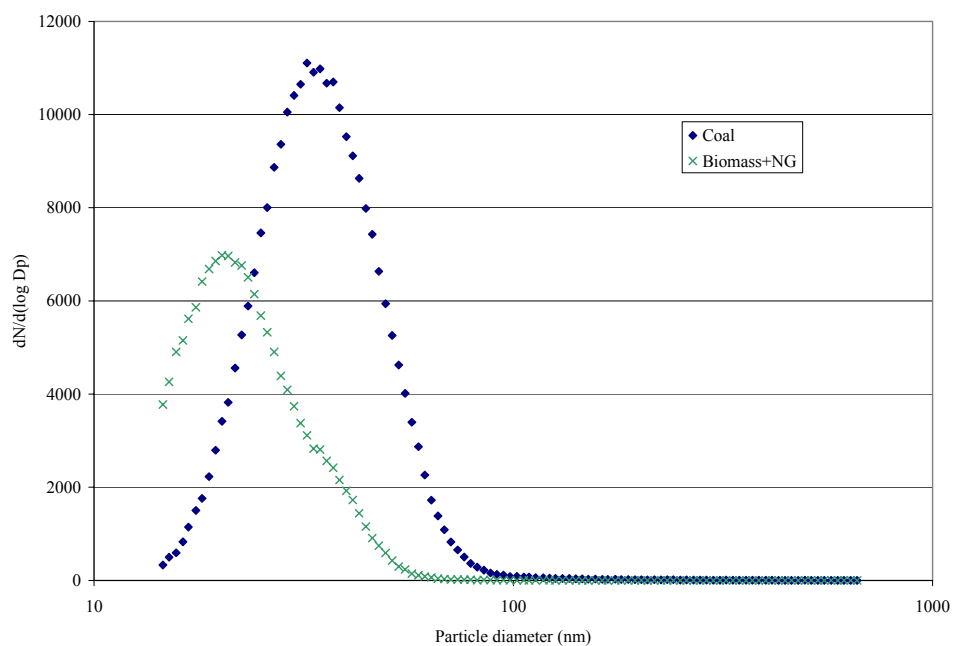


Figure 10. Comparison of particle size distributions for natural gas/biomass and Utah coal combustion.

References

Quann, R.J. Ash vaporization under simulated pulverized coal combustion conditions, Massachusetts Institute of Technology, ScD thesis, 1992.

Model substance for studies of Cr^{+6} in western coal flyash

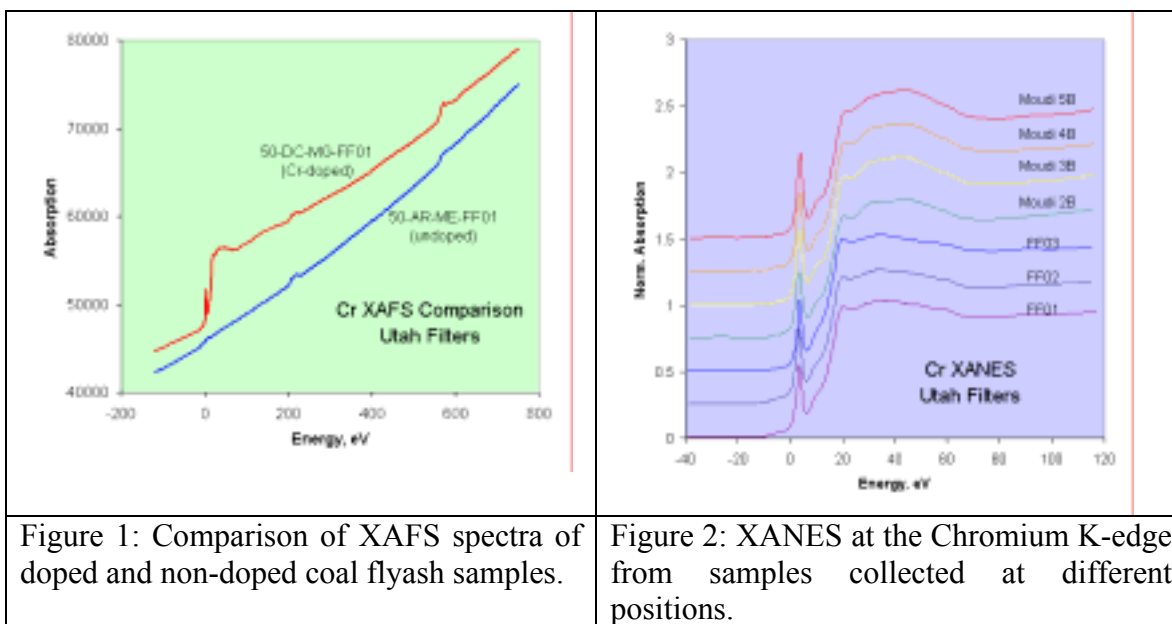
Artur Braun, Frank E. Huggins, and Gerald P. Huffman
University of Kentucky
Adel Sarofim and Kerry Kelley
University of Utah

Summary:

The presence of Cr^{+6} , the water-soluble toxic species of chromium [1], in coal flyash is a topic of significant environmental concern. To address the problem of why flyash from western U.S. coals contains significantly more Cr^{+6} than flyash from eastern U.S. coals [2], we have prepared western coal doped with significantly more chromium than is normally present and carried out combustion experiments to prepare Cr-enriched flyash samples for more detailed analytical investigation.

We have acquired one standard western coal from The Penn State Coal Sample Bank (DECS-26 Wyodak), which we doped with chromium nitrate (this contains Cr^{+3}) in a wet chemical process. The water content of this coal is about 25% and the ash residue is about 5 %.

To prevent the calcium in the coal from being washed out during the wet aqueous doping process, the solution was buffered with calcium chloride. The coal was doped so that the ash contained 1% of chromium. Doped and un-doped samples of the coal were sent to the University of Utah and combusted in a drop tube furnace described in another section of this report.



The solid combustion products were collected on filters analyzed with XANES spectroscopy at the National Synchrotron Light Source, Brookhaven National Laboratory. The results reveal that non-doped coal contains only slight traces of chromium (Figure 1), as expected by Penn State Univ.'s chemical analysis data sheet, while the doped coal contains a significant amount of Cr. Our group has a whole body of reference data and calibration spectra on chromium XAFS spectroscopy due to earlier research work [1]. About half of the chromium in the doped coal was converted from Cr^{+3} to Cr^{+6} during combustion. No attempt was made to further analyze the chromium in the un-doped coal, since the Cr content in there is in the ppm range only.

Figure 2 shows the variation of the XANES spectra at the Chromium K edge as a function of the filter or sampler position in the drop tube furnace. The prominent pre-edge peak apparent in these XANES spectra arises from Cr^{+6} and its height and area are proportional to the amount of this toxic species that is present. The percentage of the Cr present as Cr^{+6} was determined by least squares analysis of the XANES, using the calibration approach described elsewhere [1], and is summarized in the table below. It is seen that about half of the Cr in these samples is present as Cr^{+6} .

<u>XANES File</u>	<u>Filter Sample</u>	<u>%Cr(VI)</u>
CRFILTER.462S	50-DC-MG-FF01	49
CRFILTER.465S	50-DC-MG-FF02	50
CRFILTER.450S	50-DC-MG-FF03	51
CRFILTER.470S	50-DC-MG-2B Moudi	54
CRFILTER.533S	50-DC-MG-3B Moudi	52
CRFILTER.537S	50-DC-MG-4B Moudi	54
CRFILTER.529S	50-DC-MG-5B Moudi	55

The next step is to locate Cr^{+6} rich particles in the coal flyash microscopically to determine if they are correlated with the calcium or other major elements. This will be done with computer controlled scanning electron microscopy at UK and with X-ray microspectroscopy at various synchrotrons in the U.S.

References:

1. F.E. Huggins, M. Najih, and G.P. Huffman, **1999**, *Fuel*, **78**, 233-242.
2. T. Shoji, F.E. Huggins, G.P. Huffman, W.P. Linak, and C.A. Miller, *Energy & Fuels*, **16** (2001) 325-329.

XAFS Spectroscopic Characterization of Particulate Matter from Fossil-Fuel Combustion

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¹University of Kentucky, ²University of Missouri

A. Introduction.

The work described herein continues the studies initiated in the first year of the program. In this work we are using mainly spectroscopic techniques, such as XAFS and iron Mössbauer spectroscopies, to obtain an understanding of *how* various key elements occur in complex aerosol materials known collectively as particulate matter, (PM). These spectroscopic methods, with their ability to focus on a specific element and return information about the local structure and bonding, are excellent speciation methods for elements in fine aerosol materials. As described last year, we are examining PM samples from both stationary and mobile major primary combustion sources, as well as the fine ambient PM less than 2.5 μm in size ($\text{PM}_{2.5}$) (secondary PM) collected in regulation federal reference method (FRM) $\text{PM}_{2.5}$ air sampling devices.

Our overall objective in this work is to obtain information on the speciation of various elements in PM and assess the information for application to understanding health effects and for source apportionment purposes. In last year's report, results were presented of spectroscopic surveys of element speciation in residual oil fly-ash PM samples, in coal combustion PM samples, in diesel exhaust PM samples, and in ambient PM filters. The following principal findings were listed:

- Demonstration that sulfur in primary $\text{PM}_{2.5}$ from three major fossil-fuel combustion processes (residual oil combustion, coal combustion and diesel engine combustion) can exist in a variety of minor forms in addition to sulfate.
- The presence of thiophenic sulfur appears related to the amount of unburnt carbon in the primary PM sample.
- Other minor sulfur forms may be diagnostic for a specific combustion process. For example, the presence of sulfite in PM may be indicative of combustion of western US coals and the presence of bisulfate may be indicative of diesel-derived PM.
- Most metals are present in ROFA-derived and diesel-derived PM as sulfates; however, iron is an exception and may exist largely as oxide or oxyhydroxide forms.
- Coarse ROFA PM ($\text{PM}_{2.5+}$) appears to contain metal sulfides of Ni, Fe and Cu, but such sulfides are largely absent from fine ROFA PM ($\text{PM}_{2.5}$). However, their presence may be related to the lean combustion conditions under which the residual oil was combusted.
- A certain fraction of nickel in ROFA $\text{PM}_{2.5+}$ samples was found as nickel subsulfide, a reputed carcinogenic compound of nickel. Again, this may be largely due to the conditions under which the residual oil was combusted.

- Iron in coal-based PM_{2.5} tends to be more completely oxidized than that in coarse PM_{2.5+}, including within the complex spinel phase, (X²⁺)(Fe³⁺,Al,Cr)O₄, where X may be Fe, Mg, Ca, Ni, Zn, etc.
- PM samples from combustion of western US coals contain up to 30% of their Cr in the hexavalent oxidation state; Cr(VI) is not detected in PM from eastern US bituminous coals. Hexavalent Cr is both toxic and carcinogenic.
- Arsenic in all PM samples so far examined, regardless of source, exists as arsenate, in which the oxidation state is As(V). No evidence has been found for the presence of the more toxic As(III) oxidation state.
- Sulfur in PM samples from diesel exhaust is more dispersed and/or diluted in such samples from engines under load than at idle.
- XAFS experiments can be performed with reasonable success on Teflon filters used in FRM ambient air monitoring devices, as long as the sample is collected over a four-day or longer period.
- Sulfur in ambient PM_{2.5} samples appears to exist almost entirely as sulfate.
- Zinc in ambient PM_{2.5} exists as fully hydrated zinc sulfate (ZnSO₄·7H₂O); in contrast, anhydrous or only partially hydrated zinc sulfates may be present in ROFA and diesel-derived PM_{2.5}.
- Neither the sulfur nor the zinc XAFS data suggest the presence of a significant contribution from coal combustion in ambient PM_{2.5} samples collected locally.

Based on such findings, one of the main goals for the present year was to combine XAFS spectroscopy and leaching behavior for improved speciation investigation of ROFA and coal PM. This has been the main thrust of the work in the present year and has resulted in improved understanding of the speciation of a number of key elements, especially in ROFA PM. In addition, we have initiated studies on the speciation of elements in PM from jet fuel combustion and continued investigations on diesel PM and ambient PM.

B. XAFS spectroscopy and leaching behavior for improved element speciation in primary PM samples.

Although some leaching studies were initiated in last year's work, they were continued in a more systematic fashion in the present year. Three ROFA samples and one coal sample, all consisting of both PM_{2.5} and PM_{2.5+} fractions, were selected for leaching. The PM_{2.5} and PM_{2.5+} fractions of the Baseline #5 (BL5) ROFA were subjected to leaching by pentane, water, and 1N HCl acid. The leachings were done for 15 mins each at room temperature and repeated five times for each solution. The leachings were not done sequentially, but in batch mode. The leachate solutions were collected and saved for analysis, while the residues from the leachings were subjected to XAFS and other analyses. The coarse and fine fractions of two other ROFA samples, high-sulfur #6 (HS6) and low-sulfur #6 (LS6), were exposed to aqueous leaching in the course of analysis by ion chromatography (IC). The residues of the IC extractions of these four fractions were also examined by XAFS spectroscopy. Finally, the PM_{2.5} and PM_{2.5+} fractions of the Pittsburgh coal were subjected to leachings in aqueous and acid (1N HCl) solutions, using the procedures used for the BL5 ROFA PM samples. The results of the leaching studies are presented separately for the ROFA PM and coal PM samples.

B1. XAFS of leached ROFA PM samples.

(i) *Sulfur*: Sulfur XAFS investigation was conducted on all leached ROFA PM samples and the results were quite consistent from one ROFA PM sample to the next. A suite of sulfur spectra for the BL5 ROFA samples are shown in Figures 1 and 2 for the leached fine $PM_{2.5}$ and coarse $PM_{2.5+}$ fractions, respectively.

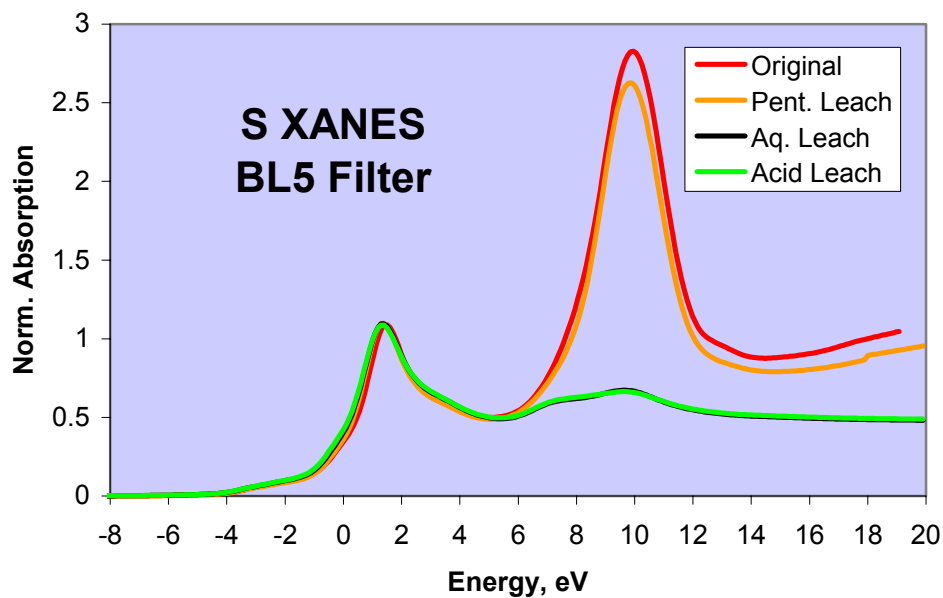


Figure 1: Sulfur XANES spectra of the $PM_{2.5}$ fraction of BL5 ROFA PM subjected to batch leachings in pentane, water, and IN HCl. Spectra are normalized to the same peak-height for the thiophene absorption at approximately 1.3 eV above the zero-point of energy for the sulfur XANES, which is taken by definition as occurring at 2472 eV.

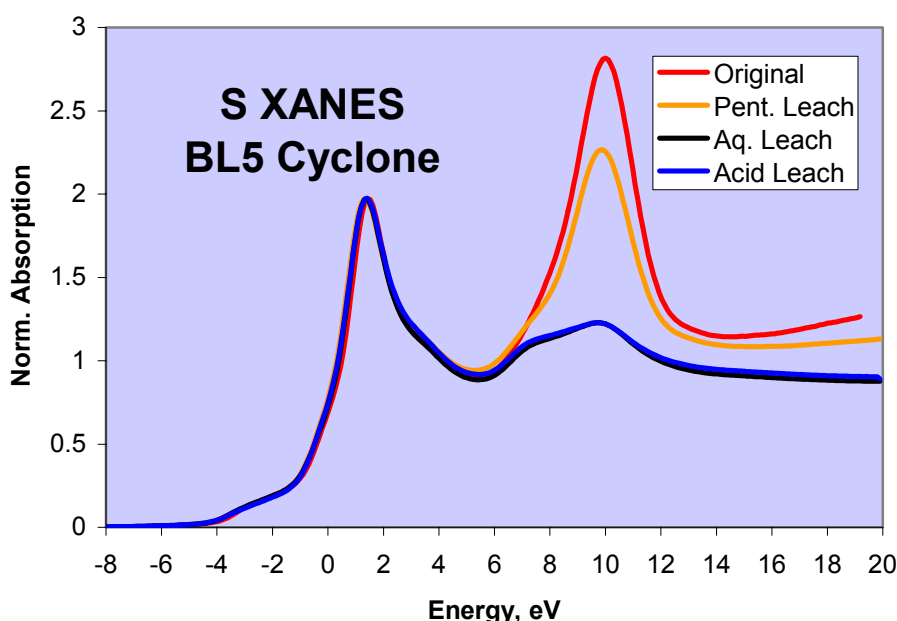


Figure 2: Sulfur XANES spectra of the $PM_{2.5+}$ fraction of BL5 ROFA PM subjected to batch leachings in pentane, water, and 1N HCl. Spectra are normalized to the same peak-height for the thiophene absorption at approximately 1.3 eV above the zero-point of energy for the sulfur XANES, which is taken by definition as occurring at 2472 eV.

The spectra of the leached ROFA PM samples show clearly that the pentane leaching has little effect on the forms of sulfur in the PM samples. However, the aqueous and acid leachings have virtually identical effects on the sulfur spectra and show that most of the sulfate sulfur can be removed from ROFA PM by either treatment. Furthermore, none of the three solutions has any effect on the reduced sulfur forms in the ROFA PM. It would appear that the elemental sulfur, thiophenic sulfur, and inorganic sulfide sulfur are largely unaffected by any of the leaching solutions attempted.

Although they were only subjected to aqueous leaching, the sulfur XANES spectra of the HS6 and LS6 leached residues show virtually identical results to those for the corresponding spectra of BL5 fractions. Almost all of the sulfate sulfur was removed by aqueous leaching, but the reduced sulfur forms were unaffected by the aqueous treatment. Hence, the behavior of all six fractions of ROFA PM subjected to aqueous leaching was identical.

The sulfur XANES spectra of the leached ROFA samples have been subjected to the calibrated least-squares fitting, described elsewhere [1,2], in order to quantify the different forms of sulfur in the leached samples. The results of this procedure are shown in Table 1 and 2 respectively for the BL5 ROFA PM and the HS6 and LS6

ROFA PM, respectively. The least-squares fitted data for the original sample, published elsewhere [3], is also shown for comparison purposes.

Table 1: Results from least-squares fitting of sulfur XANES spectra of original and leached BL5 ROFA PM residues.

BL5 ROFA PM _{2.5}	Orig.	Pent.	Aq.	Acid
Pyrrhotite	11	15	26	24
Elemental	5	5	10	11
Thiophene	24	29	60	63
Other	5	8	0	0
Sulfate	55	44	4	3

BL5 ROFA PM _{2.5+}	Orig.	Pent.	Aq.	Acid
Pyrrhotite	19	20	33	32
Elemental	8	7	8	7
Thiophene	37	44	57	58
Other	4	3	0	0
Sulfate	32	26	3	3

It can be seen from these two tables that the %S as sulfate has decreased dramatically as a result of aqueous leaching and that there has been a corresponding increase in the reduced forms of sulfur in the samples. However, there does remain some sulfur as sulfate, particularly in the HS6 and LS6 samples. Due to differences in leaching procedure, it is likely that the aqueous leaching has not been so thorough in the case of these two samples compared to that for the BL5 samples. Alternatively, it could mean that there exists some insoluble sulfates in these samples that are more abundant in the HS6 and LS6 ROFA ash. Calcium sulfates have been reported to be present in ROFA PM samples [3]. These and other alkaline earth sulfates (e.g. SrSO₄, BaSO₄) are known to be only sparingly soluble in aqueous solutions.

Table 2: Results from least-squares fitting of sulfur XANES spectra of original and leached HS6 and LS6 ROFA PM residues.

HS6 ROFA	Filter, PM _{2.5}		Cycl., PM _{2.5+}	
	Orig.	Aq.	Orig	Aq
Pyrrhotite	11	28	26	38
Elemental	5	9	9	11
Thiophene	29	46	39	40
Other	1	7	0	6
Sulfate	54	11	26	6

LS6 ROFA	Filter, PM _{2.5}		Cycl., PM _{2.5+}	
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	Orig.	Aq.	Orig	Aq
Pyrrhotite	0	0	0	0
Elemental	0	6	6	7
Thiophene	14	75	34	66
Other	2	3	2	9
Sulfate	84	17	58	19

For the BL5 samples, we have estimated the relative change in sulfur contents brought about by the leaching. This is estimated from the thiophene sulfur contents, assuming no loss of thiophene in any leaching solution. The data are presented in Figure 3. These trends should be compared to the corresponding data shown in Table 4 measured by MS-ICP by Joe Kyger and Dave Robertson at the U. Missouri. There is very good agreement for the trends exhibited by the PM_{2.5} (filter) samples, but the agreement is less good for the PM_{2.5+} (cyclone) samples and may indicate that there is a sampling problem for the PM_{2.5+} samples.

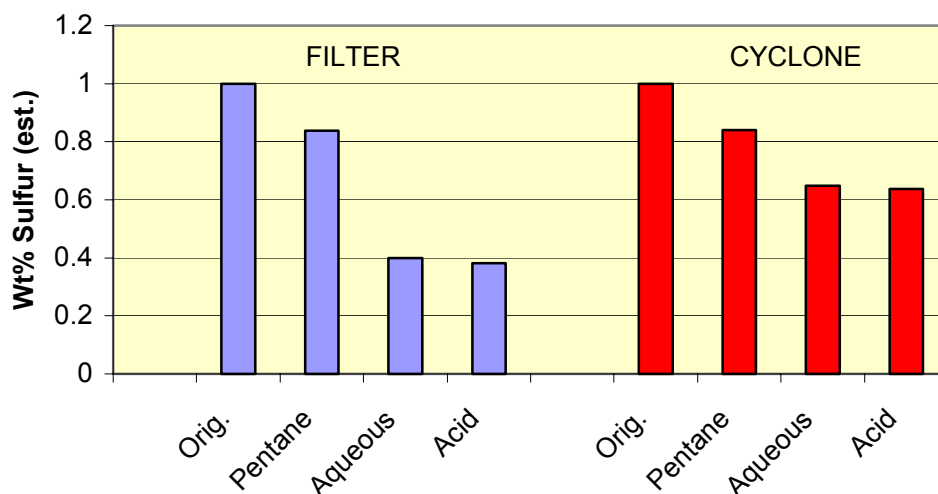


Figure 3: Estimated change in relative sulfur contents for BL5 ROFA samples as calculated from the sulfur XANES data for thiophene, assuming no loss of thiophenic sulfur in the leaching procedures.

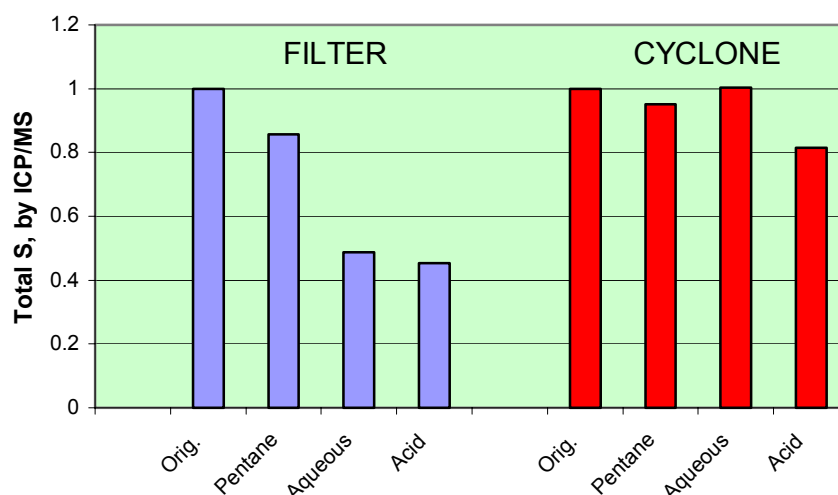


Figure 4: Relative sulfur contents measured for leached BL5 PM samples by ICP/MS. Data courtesy of J. Kyger and J. D. Robertson, U. Missouri.

(ii) Nickel: Nickel is typically the second most abundant metallic element in ROFA PM, after vanadium. In earlier work, based largely on Ni K-edge XAFS spectroscopy, we have identified the presence of nickel sulfate and nickel ferrite in fly-ash and PM samples from commercial power plants burning residual oil [4,5]. Nickel sulfide was generally absent or negligibly small in the samples from the commercial plants. However, a nickel sulfide thought to be the subsulfide Ni_3S_2 was revealed in preliminary leaching and XAFS investigations of the ROFA PM samples. This result has now been confirmed by XAFS examination of Ni in the leaching residues from the ROFA samples in more recent work that is presented here. Figures 5 and 6 show the Ni XANES spectra and Ni EXAFS/RSFs for the LS6 ROFA $\text{PM}_{2.5}$ and $\text{PM}_{2.5+}$ samples before and after aqueous leaching. It is clear that the residue phases for the two size fractions are quite different from each other. In fact, by comparison with Ni standards [4,5], they can be identified as nickel ferrite (NiFe_2O_4) and nickel sulfide, respectively, in the $\text{PM}_{2.5}$ and $\text{PM}_{2.5+}$ fractions. The HS6 ROFA samples do not show evidence for the significant presence of nickel ferrite, but a nickel sulfide phase is clearly present in the leached $\text{PM}_{2.5+}$ fraction.

The Ni XANES data for the BL5 leached ROFA samples are shown in Figures 7 and 8 for the $\text{PM}_{2.5}$ and $\text{PM}_{2.5+}$ fractions. Again, as was noted for sulfur, the pentane leaching appears to have relatively little effect on the spectra and Ni speciation. However, the aqueous and acid leaching do bring about major changes in the Ni speciation. For the BL5 $\text{PM}_{2.5+}$ fraction, the aqueous and acid leaching clearly reveal a nickel sulfide, while the nickel ferrite is somewhat revealed by the leachings, although not to the same extent as in the LS6 $\text{PM}_{2.5}$ sample.

To quantify the nickel speciation, we resorted to least-squares fitting of the nickel XANES spectra. In previous attempts of this nature [6], we had limited the least-squares fitting to only two compounds: Ni sulfate and Ni ferrite in $\text{PM}_{2.5}$ samples or Ni sulfate

and Ni sulfide in $\text{PM}_{2.5+}$ samples. However, it is naïve to expect that such a clean and clear difference in Ni speciation between $\text{PM}_{2.5}$ and $\text{PM}_{2.5+}$ samples actually exists. For this reason, then we attempted to simulate all the Ni XANES spectra using a linear least-squares fitting procedure based on all three nickel compounds that we knew to be present in these materials.

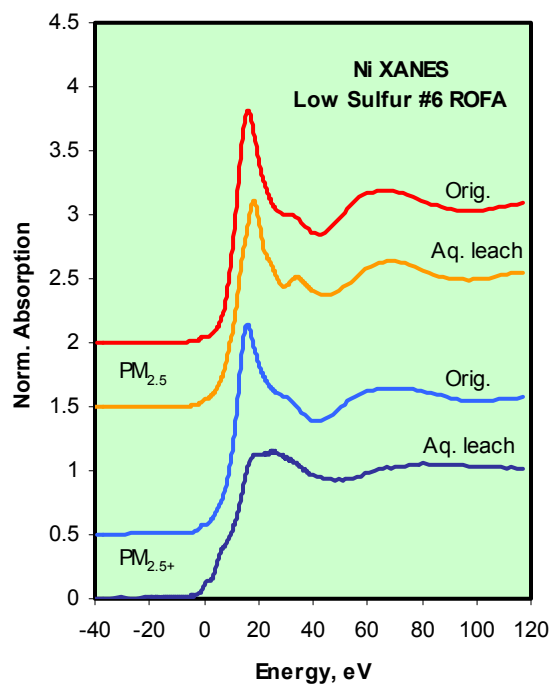


Figure 5: Ni XANES spectra for LS6 ROFA PM samples before and after aqueous leaching.

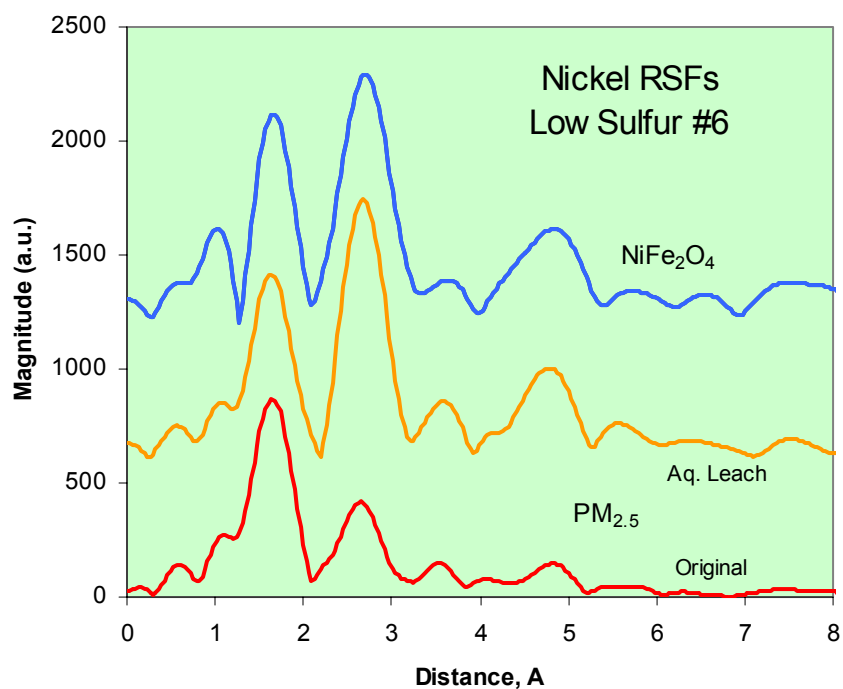


Figure 6: RSFs for Ni in LS6 ROFA PM_{2.5} sample before and after aqueous leaching. Also shown for comparison purposes is the RSF for nickel ferrite, NiFe₂O₄.

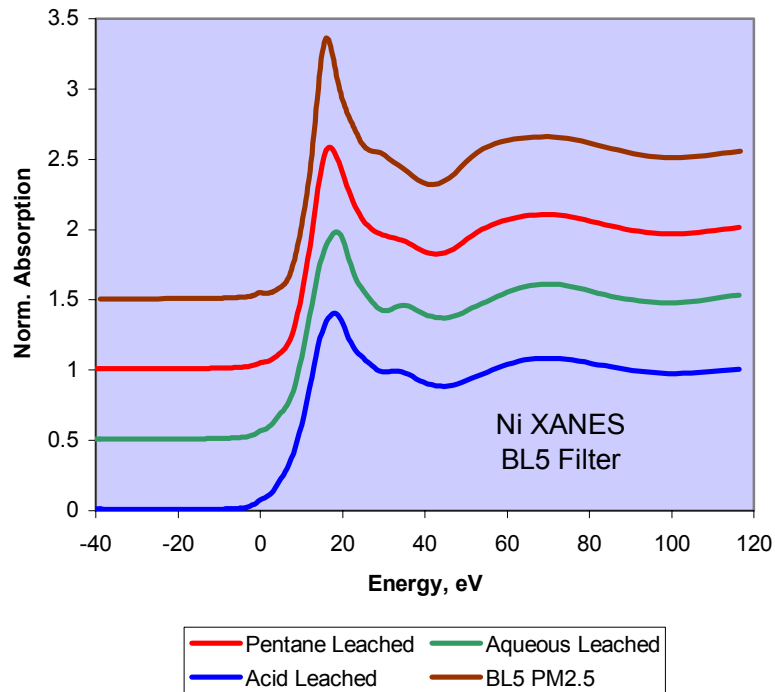


Figure 7: Ni XANES spectra for leached samples of BL5 PM_{2.5}.

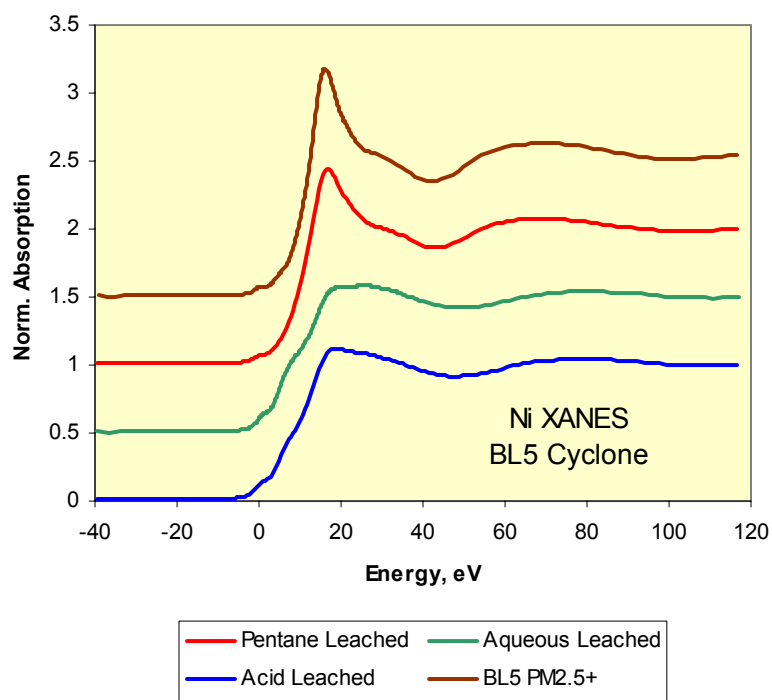


Figure 8: Ni XANES spectra for leached samples pf BL5 PM_{2.5}+

An example of the least-squares fitting of a Ni XANES spectrum from the aqueous leached BL5 PM_{2.5} sample is shown in Figure 9. Data from the least-squares fitting on the nickel speciation for all ROFA samples, both original and leached, are summarized in Table 3.

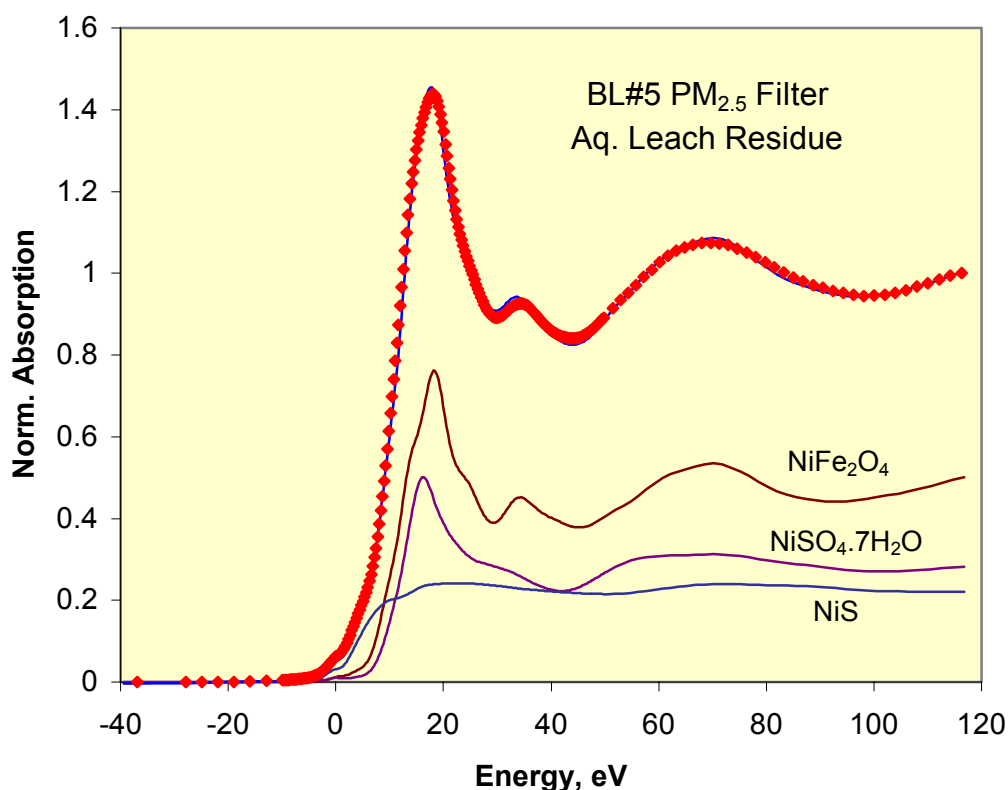


Figure 9: An example of a least-squares fit Ni XANES spectrum using the three major Ni-bearing components identified in ROFA PM samples. The three components are shown at the relative heights of their contribution to the XANES spectrum (q.v. Table 3)

The data shown in Table 3 indicate that, as expected, all three Ni compounds are indeed present in both coarse and fine PM fractions of the ROFA samples. However, it is also clear that there is a tendency for the Ni sulfide to be found in greater proportions in the coarse PM_{2.5+} fractions than in the corresponding fine PM_{2.5} fractions. Conversely, there is relatively little nickel ferrite present in the coarse fraction; indeed, for all PM_{2.5+} samples, no Ni ferrite was observed to be significant relative to a detection limit estimated to be no more than 5% of the Ni. For this Ni phase, it can be argued that it is indeed restricted to the fine PM_{2.5} fractions. For the one sample prepared in a refractory furnace (BL6R), the nickel speciation is predominantly nickel sulfate with a very minor contribution from Ni ferrite. We note also that whereas nickel sulfate is entirely removed from the PM_{2.5+} samples by aqueous leaching, nickel sulfate remains significant in a number of PM_{2.5} samples even after aqueous and acid leaching. Why nickel sulfate should be completely dissolved from coarse PM and not from fine PM would appear to be quite unlikely. It may therefore imply that what we are interpreting as nickel sulfate in the aqueous and acid leached PM_{2.5} samples may in fact be an unidentified insoluble Ni form. Furthermore, it is possible that the Ni ferrite is extremely small sized (nanoparticles) and may also be substituted by other elements so that the standard NiFe₂O₄ spectrum is not a very good match for that in the PM_{2.5} samples. However, there does

not appear to have been reported an XAFS study of nano-NiFe₂O₄, although there have been a number of Mössbauer studies of this material in nano form.[7-9].

Table 3: Summary of results from least-squares fitting of Ni XANES Spectra of original and leached ROFA PM samples .

Sample	%Ni as sulfate	%Ni as sulfide	%Ni as ferrite
LS#6 Filter	69	7	24
LS#6 Filter aq. Leach	--	13	87
LS#6 Cyclone	75	25	--
LS#6 Cyclone aq. Leach	<5	>95	<5
MS#6 Filter	87	5	8
MS#6 Cyclone	81	19	--
HS#6 Filter	89	5	6
HS#6 Filter aq. Leach	40	42	18
HS#6 Cyclone	71	25	4
HS#6 Cyclone aq. Leach	<5	>95	<5
BL#5 Filter	90	<5	10
BL#5 Filter Pent. Leach	67	9	24
BL#5 Filter aq. Leach	29	23	48
BL#5 Filter acid Leach	30	34	36
BL#5 Cyclone	82	18	--
BL#5 Cyclone Pent. Leach	66	34	--
BL#5 Cyclone aq. Leach	<5	>95	<5
BL#5 Cyclone acid Leach	<5	>95	<5
BL#6 Refractory Furnace	93	--	7

Interestingly, when we do compare the iron Mössbauer data for the BL5 ROFA PM_{2.5} sample (presented in last year's report) with that for small-particle NiFe₂O₄, there is a very strong resemblance to the spectra published by Ma et al. [7] and Sui et al. [8] for nano-NiFe₂O₄, nominally of an average particle size of about 12 nm.

Additional information on the possible particle size of Ni species in ROFA PM may be forthcoming from anomalous small-angle X-ray scattering (ASAXS). In 2002, we made some measurements by ASAXS at the Ni K-edge at the BESSERC SAXS facility at the Advanced Photon Source (APS), Argonne National Laboratory, on the leached ROFA PM BL5 and HS6 samples. The preliminary analysis of the data for the BL5 PM samples is summarized in Table 4. The first observation one makes from these data would appear at first sight to be counter-intuitive: the average particle size determined for the nickel species in the coarser PM_{2.5+} leaching residues is significantly smaller than that

determined for the finer PM_{2.5} leaching residues fractions. As part of an attempt to rationalize these results, we should recall that nickel in the residual oil is largely present as individual Ni atoms in porphyrin groups or other organically bound species. One must also recall that the Ni content of the PM_{2.5+} fraction is much less than that of the PM_{2.5} fraction and, furthermore, that the LOI for the PM_{2.5+} fraction is higher than that for the PM_{2.5} fraction, indicating that the Ni in the PM_{2.5} fraction has experienced somewhat more complete combustion. It may therefore be advanced that the agglomeration of Ni species for the PM_{2.5} fraction has progressed more than it has for the Ni in the PM_{2.5+} fraction because of just those two reasons.

Table 4: Preliminary results on Ni species size from ASAXS measurements.

<i>Leaching Residue</i>	<i>ROFA Filter, PM_{2.5}</i>		<i>ROFA Cyclone, PM_{2.5+}</i>	
	<i><R_{ave}> in nm</i>	<i>Width, σ, in nm</i>	<i><R_{ave}> in nm</i>	<i>Width, σ, in nm</i>
<i>Pentane</i>	<i>10.0 ± 0.6</i>	<i>4.6</i>	<i>6.8 ± 1.2</i>	<i>3.9</i>
<i>Aqueous</i>	<i>8.2 ± 0.2</i>	<i>3.3</i>	<i>5.7 ± 2.0</i>	<i>5.1</i>
<i>Acid (1N HCl)</i>	<i>9.6 ± 0.5</i>	<i>4.9</i>	<i>6.1 ± 0.2</i>	<i>3.5</i>

Further development of this method will be attempted because the preliminary analysis of the ASAXS data does not take into account the fact that the speciation changes from residue to residue. Whether or not this has a large influence on the derived Ni species size remains to be evaluated.

(iii) *Vanadium*: A similar approach to that developed above for Ni has been taken for the analysis of vanadium in the ROFA PM samples. From the V XANES spectra obtained from leached ROFA PM samples, we identify three main vanadium species present in most of the samples: vanadyl sulfate, $\text{VOSO}_4 \cdot x\text{H}_2\text{O}$, vanadium oxide, tentatively identified as small-particle VO_2 , and a vanadium sulfide. These components are best shown in the V XANES spectra presented in Figures 10 and 11.

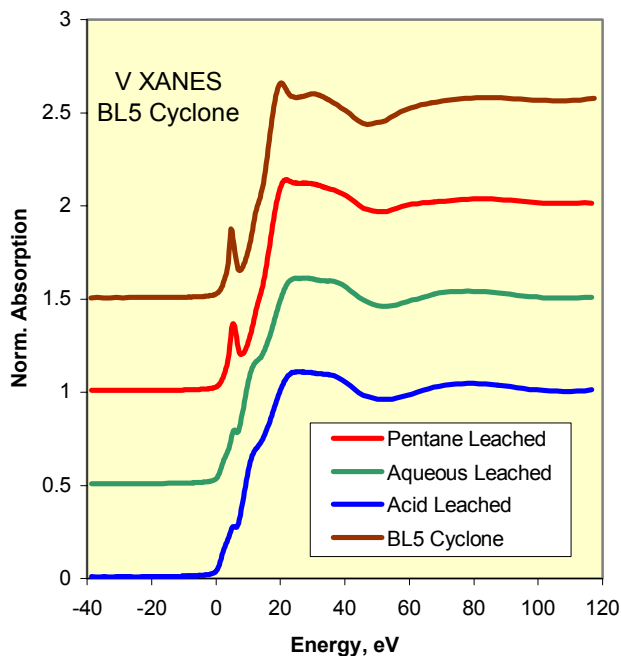


Figure 10: Vanadium XANES of original and leached BL5 $\text{PM}_{2.5+}$ ROFA.

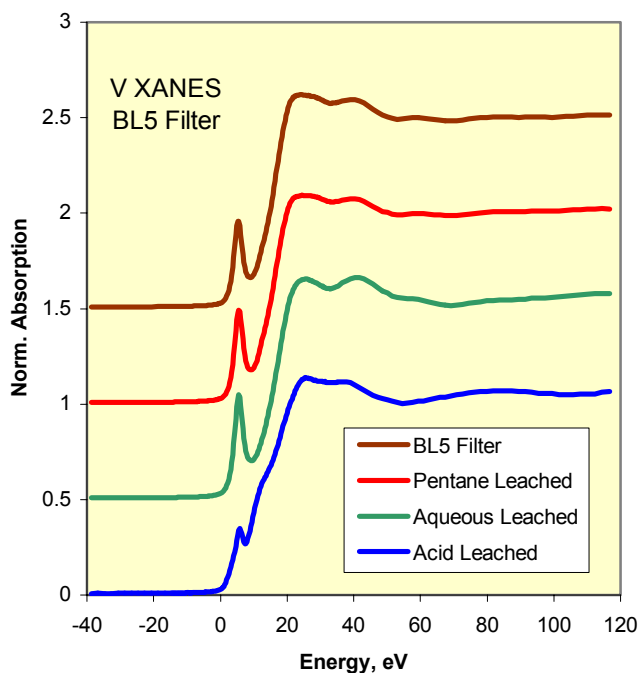


Figure 11: Vanadium XANES of original and leached BL5 $\text{PM}_{2.5}$ ROFA.

A clear distinction can be seen between the original spectra for the $\text{PM}_{2.5+}$ and $\text{PM}_{2.5}$ fractions of the BL5 PM. Based on the spectral profile, the V form dominant in the $\text{PM}_{2.5+}$ fraction is vanadyl sulfate, whereas the dominant form in the $\text{PM}_{2.5}$ fraction is believed to be VO_2 . The former spectrum, which also dominates the spectra of both the original LS6 PM fractions (Figure 12), is closely similar to that we have measured for $\text{VOSO}_4 \cdot x\text{H}_2\text{O}$ and that reported by Frank and Hodgson [10], but differs somewhat from that reported by Wong et al. [11]. For both acid leached BL5 PM fractions, a quite different spectrum is observed; a similar spectrum is seen for the aqueous leached $\text{PM}_{2.5+}$ fraction, but not for the aqueous leached $\text{PM}_{2.5}$ fraction. Instead, the latter spectrum resembles that of VO_2 , although the match is not exact as the XANES peaks for ROFA PM appear broadened in comparison for those of VO_2 . We suspect that small particle-size effects may explain the difference. The remaining vanadium form, best exemplified by the spectrum of acid-leached BL5 $\text{PM}_{2.5+}$ residue, has the shape and character of a vanadium sulfide. However, it is clearly different from that of V_2S_3 reported by Wong et al. [11] and a positive identification of this sulfide has not yet been made.

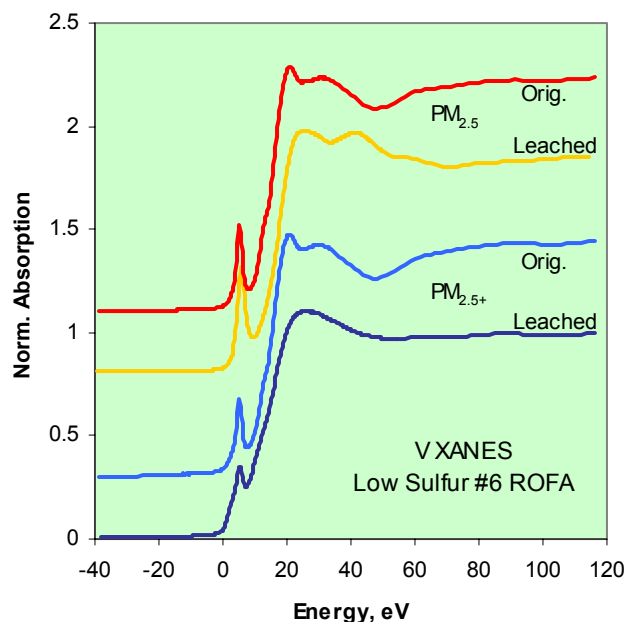


Figure 12: V XANES spectra for the original and aqueous leached LS6 PM fractions.

Despite the uncertainty of the interpretations of the spectra, however, it is clear that the vanadium XANES spectra of the ROFA PM consist mainly of the three spectral components represented by vanadyl sulfate, the vanadium oxide and vanadium sulfide. Rather than using the standard but less representative spectra for VO_2 and V_2S_3 , we chose to use the spectrum shown in Figure 10 for the acid-leached BL5 $\text{PM}_{2.5+}$ sample for the vanadium sulfide component and the spectrum shown in Figure 12 for the aqueous leached LS6 $\text{PM}_{2.5}$ sample for the vanadium oxide component. We recognize that the latter spectrum may include a minor contribution from vanadium sulfide in addition to the dominant VO_2 species, but it is unlikely that the sulfide component represents more than 10% of the vanadium in this particular residue sample.

Using these three components, the V XANES spectra of all the ROFA PM samples, original and leached, were then least-squares fit to determine the percentages of vanadium present as vanadyl sulfate, vanadium oxide (VO_2) and vanadium sulfide (V_xS_y). The results of the least-squares fitting are summarized in Table 5. Except for the original and aqueous leached HS6 PM_{2.5} samples, all the spectra could be reasonably well fit using the three components described above. For the HS6 PM_{2.5} samples, it would appear that an additional vanadium species must be present, although the vanadium oxide is clearly a major component. For these spectra, we note that the pre-edge peak is larger than that in VO_2 and the absorption edge appears to be shifted to slightly higher energy; such differences are suggestive of the presence of V in the pentavalent oxidation state, probably in the form of a vanadate. CCSEM data (see section.....) suggest the possible presence of other vanadium containing phases for the HS6 PM_{2.5} sample, including phases of composition Ca-V-S and Na-V-P. Possibly significant amounts of the vanadate anion (VO_4^{3-}) can substitute for SO_4^{2-} or PO_4^{3-} anions in sulfate or phosphate phases.

Table 5: Results of least-squares fitting of vanadium XANES spectra of original and leached ROFA PM samples.

Sample	%V as sulfate	%V as oxide	%V as sulfide
LS#6 Filter	70	28	2
LS#6 Filter aq. Leach	--	100	--
LS#6 Cyclone	82	--	18
LS#6 Cyclone aq. Leach	--	50	50
MS#6 Filter	78	11	11
MS#6 Cyclone	82	--	18
HS#6 Filter	**	>50**	**
HS#6 Filter aq. Leach	**	>80**	**
HS#6 Cyclone	20	67	13
HS#6 Cyclone aq. Leach		60	40
BL#5 Filter (1999)	27	73	--
BL#5 Filter (2002)	0	100	0
BL#5 Filter Pent. Leach	--	95	5
BL#5 Filter aq. Leach	--	90	10
BL#5 Filter acid Leach	--	39	61
BL#5 Cyclone (1999)	72	--	28
BL#5 Cyclone Pent. Leach	33	34	33
BL#5 Cyclone aq. Leach	--	10	90
BL#5 Cyclone acid Leach	0	0	100
BL#6 Refractory Furnace	100	0	0

** Inadequately fit by the three phases included in fitting scheme. Presence of an additional compound (a vanadate?) is suspected (see text).

Another observation relates to the spectra of the original sample of BL5 PM_{2.5}, measured three years apart. As indicated in Table 5 and in Figure 13, these spectra are quite different. The data suggest that the vanadyl sulfate present initially has hydrolyzed into vanadium oxide during storage. A similar mechanism would also explain the difference in vanadium speciation between the original BL5 PM_{2.5+} sample and the pentane-leached sample measured three years later. Note also that vanadium oxide is only observed for those PM_{2.5+} samples subjected to leaching in 2002. None of the spectra of the original PM_{2.5+} samples measured in 1999 indicate the presence of significant vanadium oxide. All of these observations can be explained by the conversion of vanadyl sulfate into vanadium oxide during the course of the three years. Note that vanadium oxide *is* observed for the original PM_{2.5} samples and that no vanadyl sulfate is observed for any leached PM_{2.5} sample measured in 2002. These observations suggest that the conversion of vanadyl sulfate to oxide was already well underway when the original samples were first measured in 1999. These observations are also consistent with the difference in particle size between the PM_{2.5} and PM_{2.5+} samples (the smaller particle-size PM_{2.5} samples would be expected to hydrolyze more rapidly than the coarser PM_{2.5+} samples).

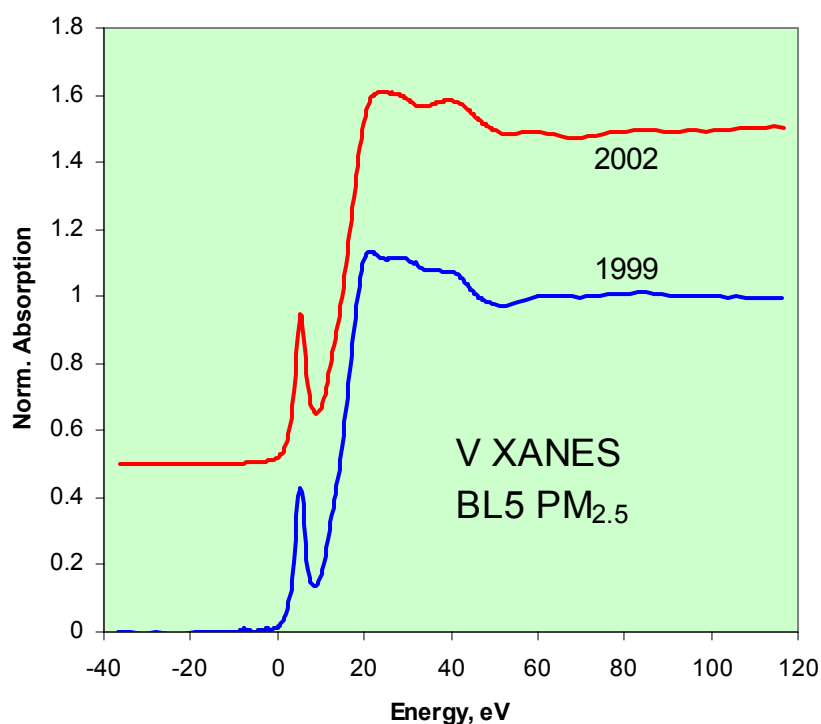


Figure 13: Comparison of V XANES spectra for BL5 ROFA PM_{2.5} taken 3 years apart.

(iv) *Iron*: Leaching data for iron in HS6 PM, LS6 PM, and BL5 PM_{2.5} ROFA samples are shown in Figures 14, 15 and 16, respectively. In comparison to nickel and vanadium, there is much less change in the overall spectrum as a result of leaching and this is also seen in analytical data for the leached samples also. Much smaller fractions of iron are removed by the different leaching solutions than is observed for Ni or V. Our

initial conjecture [3,6] that iron was present largely in the form of a ferric sulfate appears to be incorrect; rather, as already discussed for Ni, significant fractions of the iron appear to be present in the form of Ni ferrite, NiFe_2O_4 , particularly in the fine $\text{PM}_{2.5}$ fractions. Typically in analyses of ROFA PM, it is found that the Fe content is significantly less than that of Ni, and therefore, even though only a small fraction of the Ni may be present as Ni ferrite, significant amounts of the iron may be accounted for by this phase given the 1:2 atomic ratio of Ni:Fe in the ferrite phase and the lower content of iron in the ROFA PM. In this regard, we have also already noted that the Mössbauer spectrum of Fe in the BL5 $\text{PM}_{2.5}$ sample is closely similar to that exhibited by nano-particles of nickel ferrite.

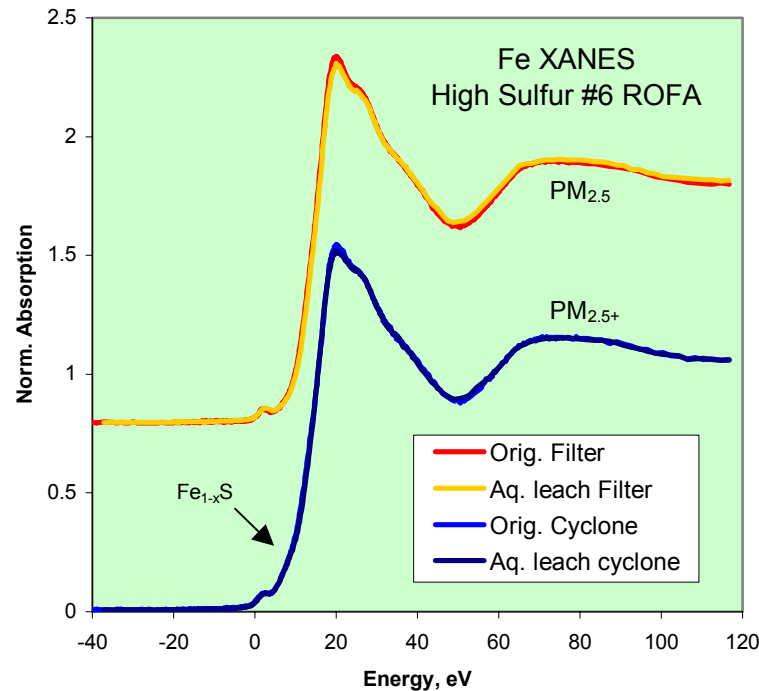


Figure 14: Fe XANES spectra of HS6 PM samples. Note the close similarity of the spectral traces for the original PM samples and those of the corresponding aqueous leached samples.

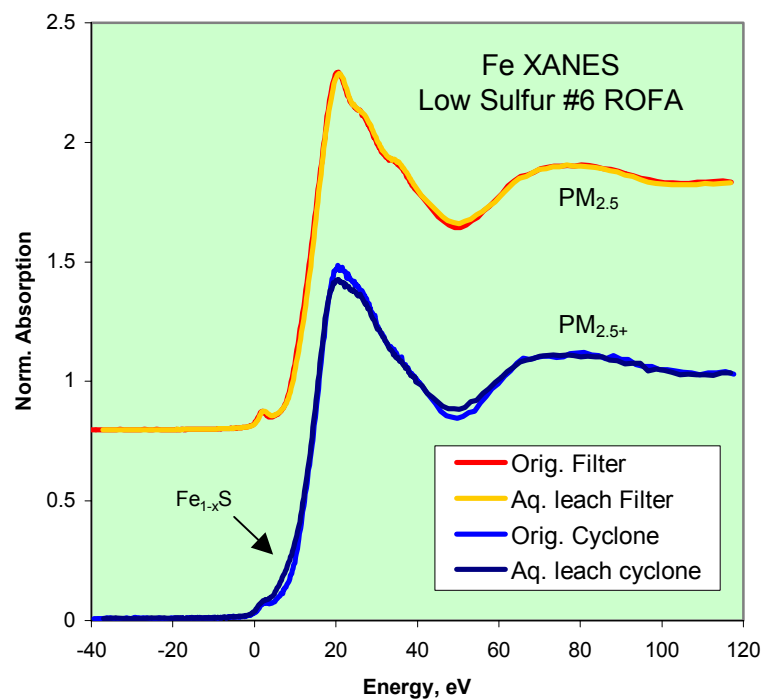


Figure 15: Fe XANES spectra of LS6 PM samples. Note the close similarity of the spectral traces for the original PM samples and those of the corresponding aqueous leached samples.

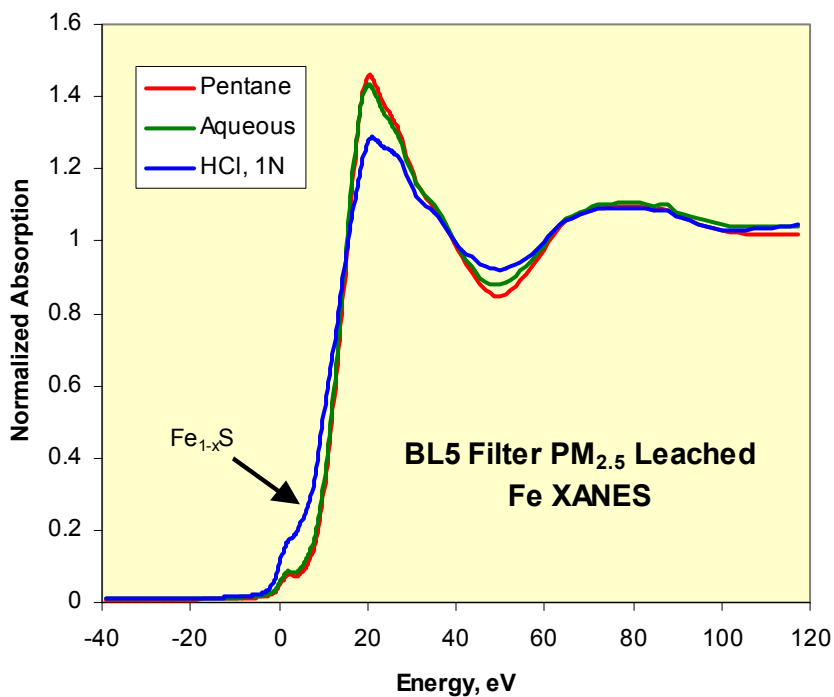


Figure 16: Fe XANES spectra of leached BL5 PM_{2.5} residues. Note the close similarity of the spectral trace for the pentane-leached residue and that of the aqueous leached residue.

It is clear from Figures 14-16 that aqueous leaching has virtually no effect on the iron speciation and this observation confirms that there is no readily soluble iron sulfate phase present in the PM. The Mössbauer data reported previously indicate that the presence of ferrous iron in ROFA PM samples is negligible. Hence, we need be concerned only with ferric iron phases. However, there are numerous different ferric-bearing sulfates of varying solubilities known to form in nature [12]. A significant number (~15) of these sulfates only involve ferric iron, sulfate anions (SO_4^{2-}), hydroxyl ions (OH^-), and waters of hydration and can be represented by the general formula: $(\text{Fe}^{3+})_x(\text{SO}_4^{2-})_y(\text{OH})_z \cdot n\text{H}_2\text{O}$; however, the majority of these are reasonably soluble in water and nearly all ferric sulfates are soluble in dilute HCl. Hence, the likelihood of significant iron sulfate being in these samples appears to be low.

The Mössbauer spectrum of BL5 $\text{PM}_{2.5+}$ indicates the presence of magnetite and possibly hematite, rather than Ni ferrite, in this sample; however, the data are not of high quality because of their low iron content. Further Mössbauer spectra will be attempted on the leached fractions of these samples to try and resolve further these issues of the iron speciation.

Iron-bearing sulfide is clearly present in the BL5 PM samples; its presence is revealed by acid leaching. Comparison of the $\text{PM}_{2.5}$ and $\text{PM}_{2.5+}$ iron XANES spectra also shows a low-energy shoulder in the $\text{PM}_{2.5+}$ fractions that arises from iron sulfide.

In summary, the iron speciation in ROFA PM samples appears to consist of largely iron oxide and sulfide phases. Much of the iron in $\text{PM}_{2.5}$ fractions can be accounted for by its occurrence in the spinel phase, nickel ferrite, whereas other iron oxides, magnetite and possibly hematite are more prevalent in $\text{PM}_{2.5+}$ samples. Iron sulfide appears to be a minor component of $\text{PM}_{2.5+}$ fractions and probably is also present in most $\text{PM}_{2.5}$ fractions as well, in similar fashion to what we have seen for V and Ni sulfides.

(v) Other Elements: Both zinc and copper in ROFA PM have also been examined by leaching and XAFS technique. Representative spectra are shown in Figures 17 and 18.

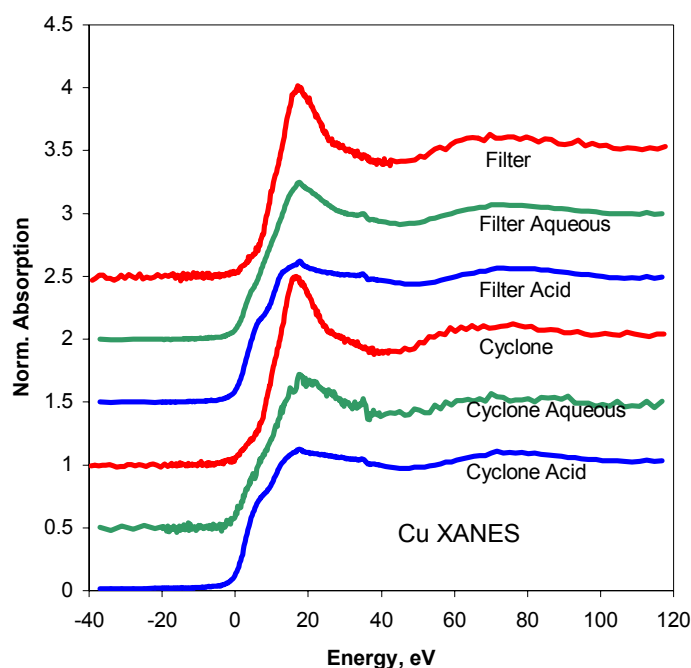


Figure 17: Cu XANES spectra of residues of leached BL5 ROFA PM fractions.

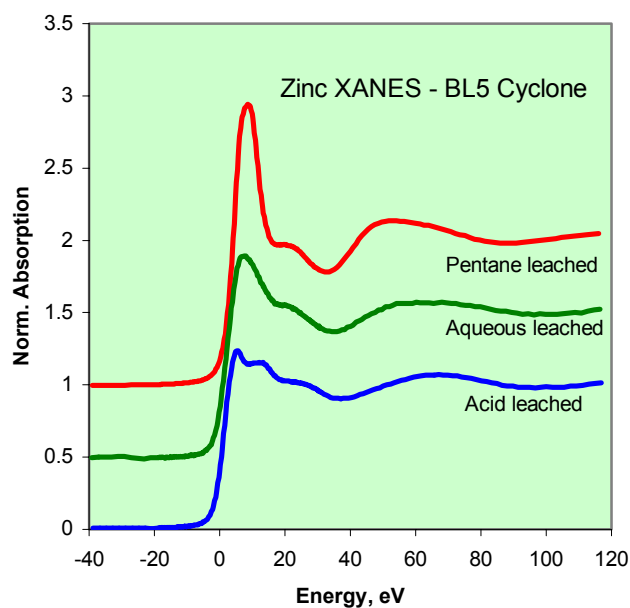


Figure 18: Zn XANES spectra of residues of leached BL5 ROFA $PM_{2.5+}$ fractions.

Both elements exhibit similar behavior to that seen for other elements. Copper sulfate and zinc sulfate dominate the spectra of the original samples and these divalent sulfates are removed by aqueous and more completely by acid leaching. In the case of copper, copper sulfide is revealed as the dominant insoluble copper phase in both BL5 acid-leached $PM_{2.5}$ and $PM_{2.5+}$ fractions, whereas zinc sulfide (ZnS) is revealed in the acid-leached BL5 $PM_{2.5+}$ residue and the aqueous-leached HS6 $PM_{2.5+}$ residue. Zinc ferrite

(ZnFe_2O_4) for the BL5 acid-leached $\text{PM}_{2.5}$ residue and zinc oxide (ZnO) for the LS6 aqueous-leached $\text{PM}_{2.5}$ residue were identified.

The XANES spectra of both Cu and Zn in aqueous-leached residues of most ROFA PM samples appear to exhibit mixed assemblages of the sulfate and other phases. For example, the spectra of the aqueous-leached residues shown for Cu in Figure 17 and for Zn in Figure 18 appear to be a mixture of the sulfate and sulfide. Least-squares fitting of the XANES spectra is planned for these elements.

Previous work reported in last year's report showed that the arsenic concentration of the LS6 samples was significantly higher than the other samples investigated. Hence, the aqueous leached residues of these samples were investigated at the As K-edge. As XANES spectra are shown in Figure 19 for the two original LS6 PM samples and the LS6 aqueous leached $\text{PM}_{2.5}$ residue. The corresponding LS6 $\text{PM}_{2.5+}$ residue exhibited virtually no spectrum at all.

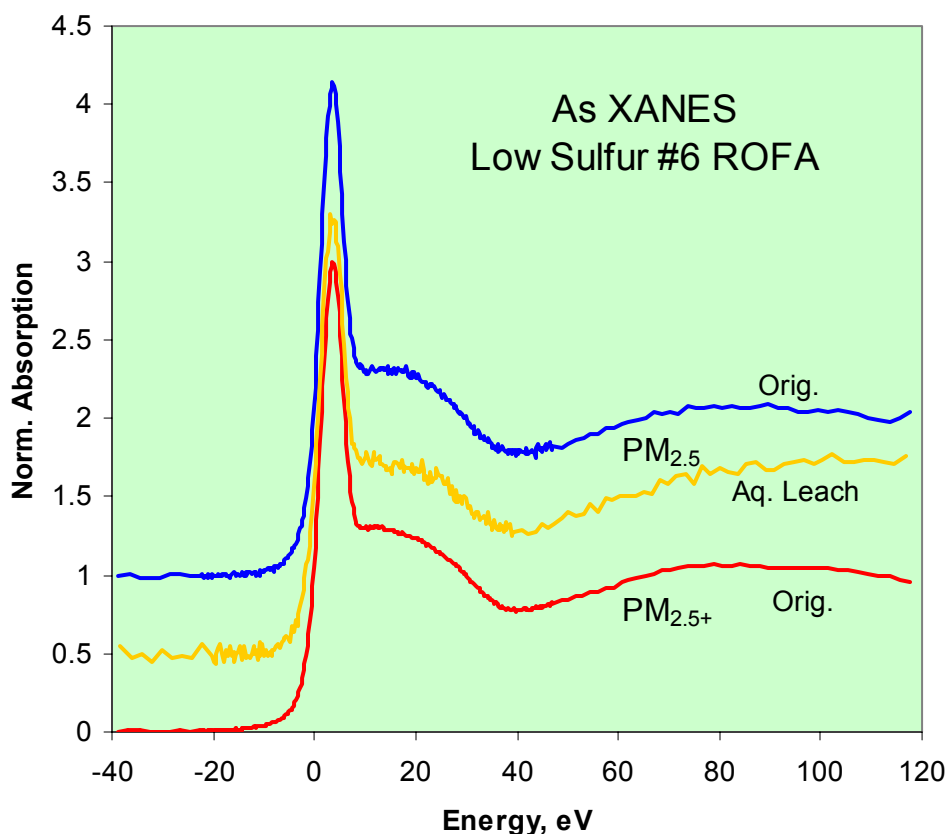


Figure 19. As XANES spectra of the aqueous leached residue the LS6 PM samples.

The BL5 samples subjected to aqueous and acid leaching showed similar results to As in LS6 ROFA PM. The BL5 $\text{PM}_{2.5+}$ leached residues showed quite weak As XANES spectra, especially the acid leached sample, whereas the BL5 $\text{PM}_{2.5}$ leached residues exhibited a strong spectrum for the aqueous leached $\text{PM}_{2.5}$, but virtually no spectrum for the acid leached $\text{PM}_{2.5}$. This suggests that the $\text{PM}_{2.5}$ samples contain two different

arsenates; one that is soluble in H₂O; the other not but which is soluble in HCl acid. In contrast, the PM_{2.5+} samples contain just the arsenate that is soluble in H₂O.

(vi) Conclusions on metal speciation in ROFA PM: Although some minor details remain to be resolved, it is clear that most metals in ROFA PM are present as some combination of sulfate, oxide, and sulfide species. The major exception is iron, which does not appear to form sulfates significantly, but rather occurs virtually entirely as ferric spinels and/or other ferric oxides and iron sulfide. Sulfide phases tend to be more prevalent for most metals in the coarser PM_{2.5+} fractions, whereas oxide phases are more prevalent in the smaller particle size PM_{2.5} fractions. Cu (and perhaps also Pb) is an exception in that there is little evidence for oxide phases in either size fraction and Cu sulfide is abundant in both size fractions. There is some evidence, from Mössbauer spectroscopy, to suggest that the oxide phases, particularly the Ni ferrite, are exceedingly fine in particle size (~ 10 nm). However, preliminary data from ASAXS measurements at the Ni K absorption edge indicate that all nickel phases are exceedingly small (<10 nm) and more so for the coarser PM_{2.5+} fraction.

Although this XAFS investigation of leached residues appears to resolve many of the questions regarding the speciation of sulfur and major metals in ROFA PM, there are a number of loose ends that remain to be examined and resolved. These include:

- XAFS investigation of nanocrystalline oxides, such as NiFe₂O₄ or VO₂, not only to complement other studies performed on these materials, but to establish also what information about nanocrystalline materials might be obtained from XAFS spectroscopy that can be applicable to the major questions surrounding PM.
- The ASAXS investigation needs to be repeated (i) on other ROFA samples and (ii) with other elements (e.g. V) to see if the preliminary conclusions reached herein for Ni are also found in other situations. In addition, more fundamental studies need to be done to establish exactly what the parameters derived from the fitting of the ASAXS data mean.
- Why does iron not exhibit the formation of sulfates? How does the nickel ferrite form?
- Why do oxides occur predominantly in the PM_{2.5} fractions and much less so in the PM_{2.5+} fractions? Conversely, why are sulfides more prevalent in the PM_{2.5+} fraction?

Such investigations would be valuable for understanding the formation, structure and speciation of PM samples,

C. Coal-based PM

As for ROFA PM, experiments for coal-based PM have concentrated on the effects of leaching. However, it was found that metals in the coal-based PM were much less sensitive to leaching than the ROFA PM, which is to be expected, given the much higher quantities of aluminosilicates in the ash. Such aluminosilicates tend to react with metals to form insoluble aluminosilicate phases or glass phases, neither of which is soluble in aqueous or acidic solutions. However, both S and As did show significant changes upon leaching. Some results are presented here. Only one coal has been investigated in detail and that is the Pittsburgh coal, as it is the coal of which we have most quantity of the two PM fractions. The PM samples of this coal were subjected to both aqueous and acid leaching, following the procedure outlined above for the BL5 ROFA PM.

(i) *Sulfur*: Sulfur XANES of the leached Pittsburgh PM samples are shown in Figures 20 and 21 for the PM_{2.5} and PM_{2.5+} samples, respectively. Significant changes are seen when the S XANES spectra of the leached PM residues are compared with that of the original PM sample. For both PM samples, but more spectacularly for the PM_{2.5} fraction, there is a significant reduction in sulfate content, while the reduced forms of sulfur, thiophenic and elemental sulfur forms, are largely unaffected by the leaching treatments. The XANES data have been least-squares fit to different sulfur forms; the results are tabulated in Table 6.

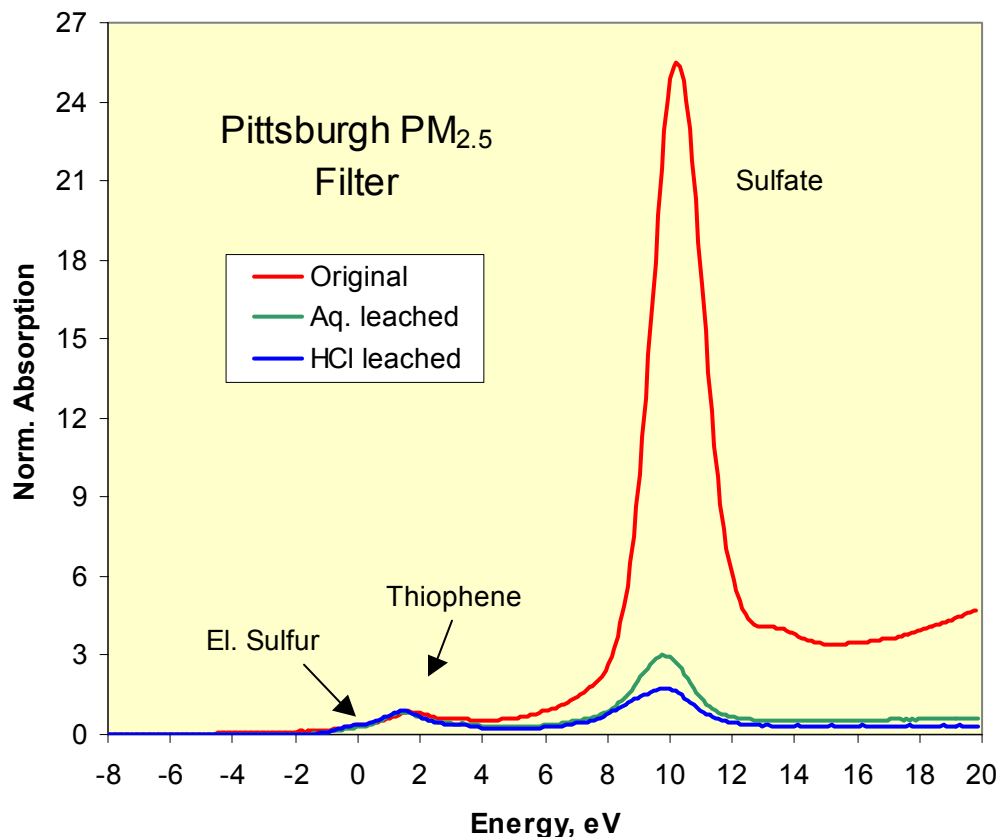


Figure 20: Sulfur XANES spectra of leached residues of Pittsburgh PM_{2.5}.

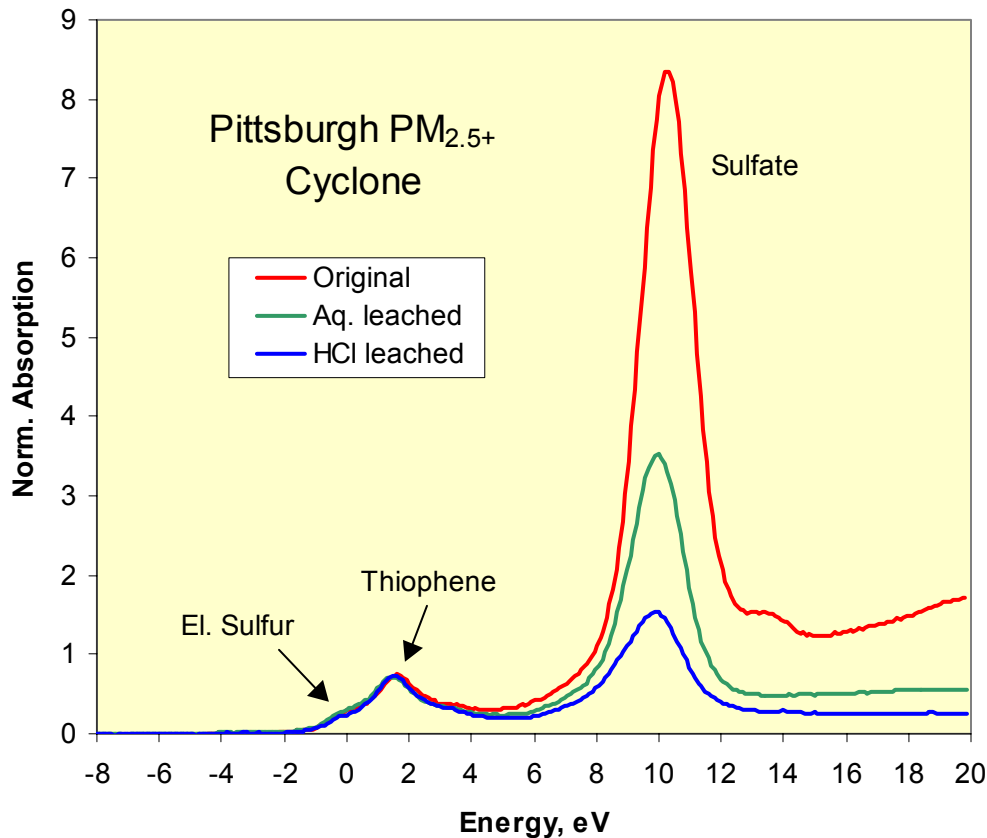


Figure 21: Sulfur XANES spectra of leached residues of Pittsburgh PM_{2.5+}.

Table 6: Least-squares fitting for Sulfur XANES of leached Pittsburgh PM Residues

Sample	Elemental S	Thiophenic S	Sulfone	Sulfate
Pittsburgh Filter PM _{2.5}	1	4	--	96
Pittsburgh Filter Aq. Leach	6	28	1	64
Pittsburgh Filter Acid leach	13	37	11	40
Pittsburgh Cyclone PM _{2.5+}	3	10	--	87
Pittsburgh Cyclone Aq. leach	7	20	1	71
Pittsburgh Cyclone Acid leach	10	38	5	48

Based on these results and assuming that the reduced sulfur forms are retained completely during the leaching, we can estimate that aqueous leaching removes about 85% and 55% of the total sulfur from the PM_{2.5} and PM_{2.5+} samples, respectively. Acid leaching is even more effective as it removes about 92% and 75% of the total sulfur from the PM_{2.5} and PM_{2.5+} samples, respectively. There is a small peak at about 13 -14 eV that is clearly seen in the S XANES spectra of the original PM samples. This peak is not present in the leached residues and indicates that the sulfates that remain in the residues

after leaching are different from the one that has been removed by leaching. Hence, we can conclude that there are sulfates in the Pittsburgh PM of different solubilities. Compilations of sulfate XANES spectra have been presented in the literature [13,14] from which we might attempt to identify the sulfates involved in the leaching. However, a sufficient number of sulfate spectra have not yet been published for such comparison to be a reliable means of identifying sulfate spectra. However, it is likely that sulfates of alkaline earth metals (Ca, Sr, Ba), given their relative insolubilities, would be good candidates for the sulfates left in the residues.

(ii) *Arsenic*: Arsenic is another element that shows quite dramatic reductions in content in the Pittsburgh coal PM samples as a consequence of leaching. Arsenic XANES spectra for Pittsburgh PM samples are shown in Figures 22 and 23 for the PM_{2.5} and PM_{2.5+} fractions, respectively. The As XANES spectra for the aqueous leached residue and original sample are quite similar for both PM fractions; however, the spectra of the acid leached residues show the clear presence of As³⁺ based on the broadened profile of the white-line peak at about 3-4 eV and the development of a shoulder on the low-energy side of the arsenate peak. This broadening is seen more clearly for the acid-leached PM_{2.5} residue than for the PM_{2.5+} residue. The presence of the As³⁺ shoulder is more clearly developed in the derivative spectra for the PM_{2.5} residues and sample shown in Figure 24. To try and quantify the amounts of the two different oxidation states in the PM samples, least-squares fitting of the As XANES spectra was undertaken. The data shown in Table 7 represent area ratios for the two oxidation states of arsenic. A calibration curve relating the area ratios to the ratios of As(III) to As(V) has not yet been developed; hence, the results in Table 7 are likely to under-represent somewhat the As(III) contents. Significant improvements in the fitting were obtained by going to a two-peak fit for all the samples, even for the original samples which contain less than about 10% of the arsenic in the trivalent state.

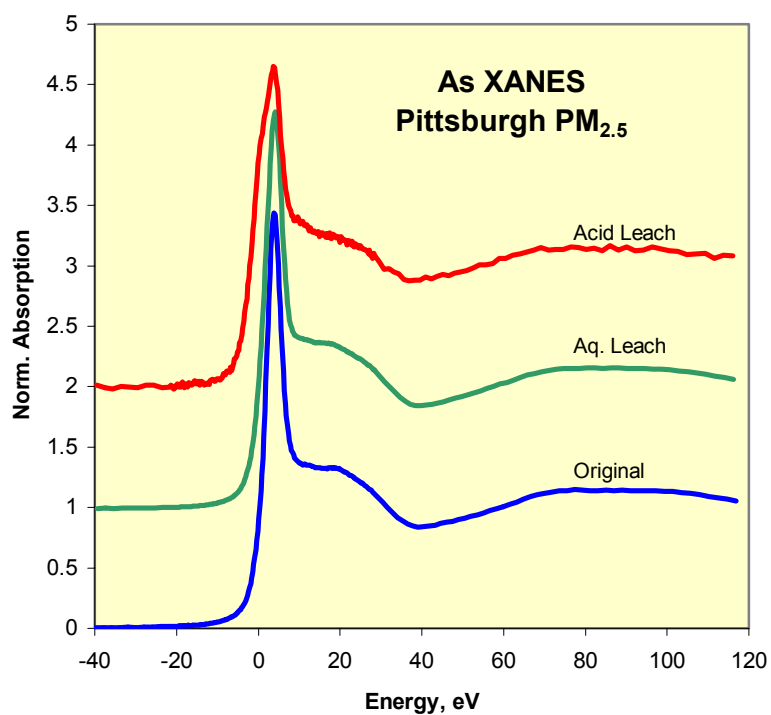


Figure 22: As XANES spectra of leached PM_{2.5} residues and original PM_{2.5} sample.

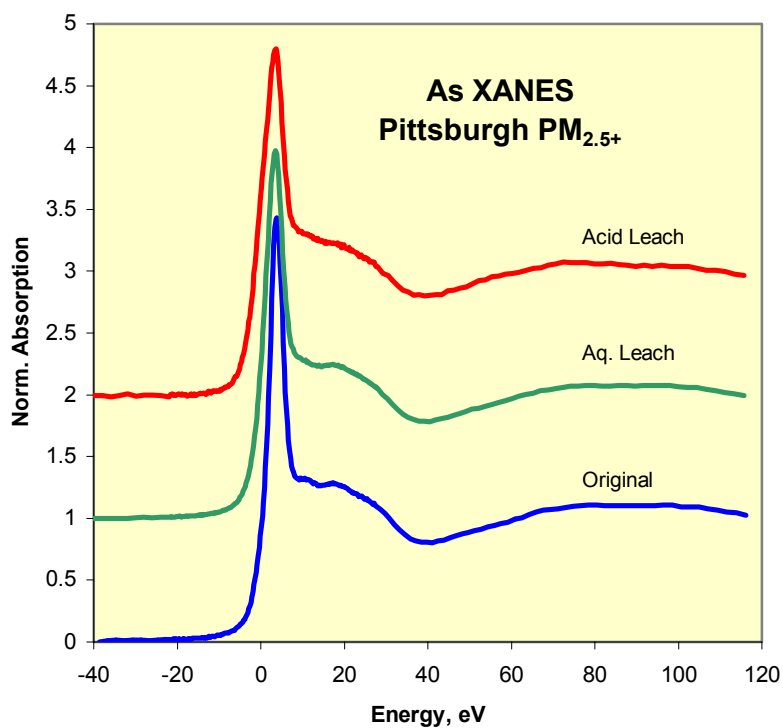


Figure 23: As XANES spectra of leached PM_{2.5+} residues and original PM_{2.5+} sample.

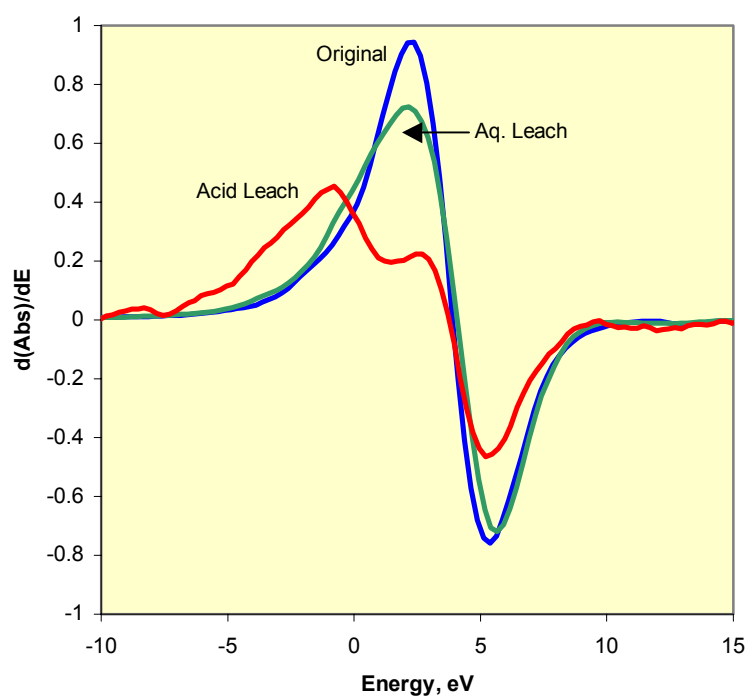


Figure 24: First derivative As XANES spectra of leached $PM_{2.5}$ residues and original $PM_{2.5}$ sample, emphasizing the asymmetric shoulder structure that results from the presence of As(III).

Table 7: Speciation results for As in leached and original Pittsburgh fly-ash PM fractions

	As(III)	As(V)
Pittsburgh Filter $PM_{2.5}$	7	93
Pittsburgh $PM_{2.5}$ Aq. Leached	7	93
Pittsburgh $PM_{2.5}$ Acid Leached	39	61
Pittsburgh Cyclone $PM_{2.5+}$	3	97
Pittsburgh $PM_{2.5+}$ Aq. Leached	11	89
Pittsburgh $PM_{2.5+}$ Acid Leached	28	72

Based on these results, the acid-leached PM samples contain about 30-50% of the As in the trivalent state, whereas the original sample and aqueous leached sample contain no more than about 10% As as As(III). However, given the significantly enhanced toxicity of As(III) relative to As(V), even the presence of 10% As(III) will greatly enhance the health threat posed by arsenic in the PM. Without leaching, such minor but health-wise important As(III) forms would have been overlooked.

(iii) *Zinc*: Like other bituminous coals, zinc in the Pittsburgh PM fractions gives a distinctive XANES spectrum, which we may interpret [15] as arising predominantly from zinc ferrite, ($ZnFe_2O_4$). As shown in Figure 25, aqueous leaching has little or no effect on the characteristic profile XANES profile in comparison to that reported previously for

the original coal PM sample [15]. However, acidic leaching does change the spectral appearance significantly.

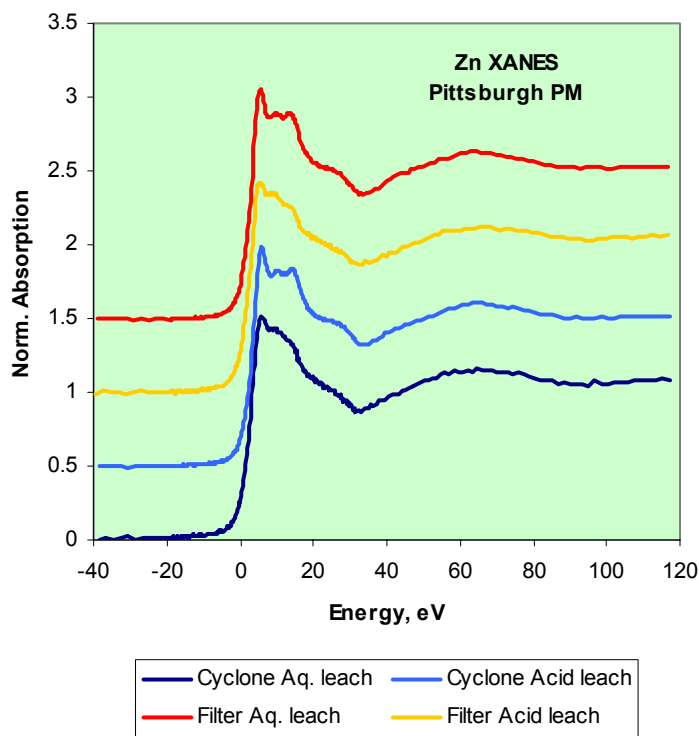


Figure 25: Zinc XANES spectra of aqueous and acid-leached Pittsburgh PM residues. It is likely that there may be various types of or a range of composition for zinc spinels formed in PM ash and that certain compositions near zinc ferrite are soluble in acid, but not in aqueous solutions. Other spinel compositions may be more resistant to acid leaching. Alternatively, the zinc in the acid residue may be present in an unidentified aluminosilicate or glass. Regardless, the zinc is in four-fold coordination based on the appearance of the XANES spectra of the acid-leached residues.

D. PM from Jet test engines at Wright-Patterson AFB

Four samples of particulate matter were collected from jet engines at Wright-Patterson Air Force Base on silica filters and returned to Kentucky for XAFS survey. To date, only sulfur and iron XAFS studies have been attempted on these samples, except for one sample that was also subjected to Cr XAFS spectroscopy. The sulfur XANES data (Figure 26) reveal that almost all of the sulfur is present as sulfate in all four samples; however, some minor amounts of thiophene and sulfoxide appear also to be present, especially for sample Jet PM 34, which exhibited the S XANES spectrum with the best signal/noise ratio. However, even taken together, these minor forms of sulfur do not amount to more than 10% of the overall sulfur in the sample.

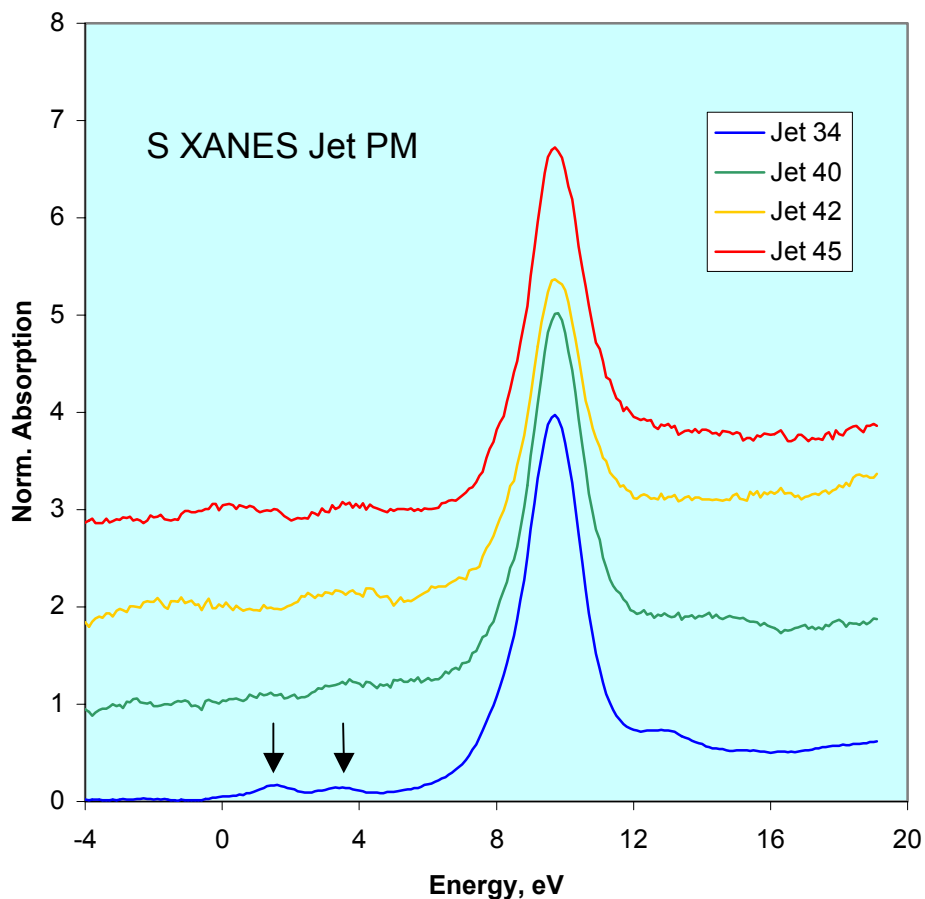


Figure 26: S XANES spectra of PM from jet engines collected on a silica filter. The peaks at 10 eV arise from sulfate sulfur; minor peaks indicated at about 1.3 and 3.2 eV in lowest spectrum arise from thiophene and sulfoxide forms, respectively.

The iron XANES spectra are shown in Figure 27. The corresponding EXAFS data were a little too weak to give consistent RSFs and are not reported. The Fe XANES spectra are all very similar, although there is some very minor variation noted for the pre-edge peak and there is a variation in signal/noise ratio reflecting a variation in iron content. The shape of the pre-edge peak and the overall spectrum are indicative of Fe(III), largely in four-coordination. The single Cr XANES spectrum obtained for sample Jet PM 34 was very noisy. However, the Cr XANES profile is indicative of Cr(III) sulfate, when compared with our database of Cr standards [16]. Additional elements (e.g. zinc) will be examined in the near future.

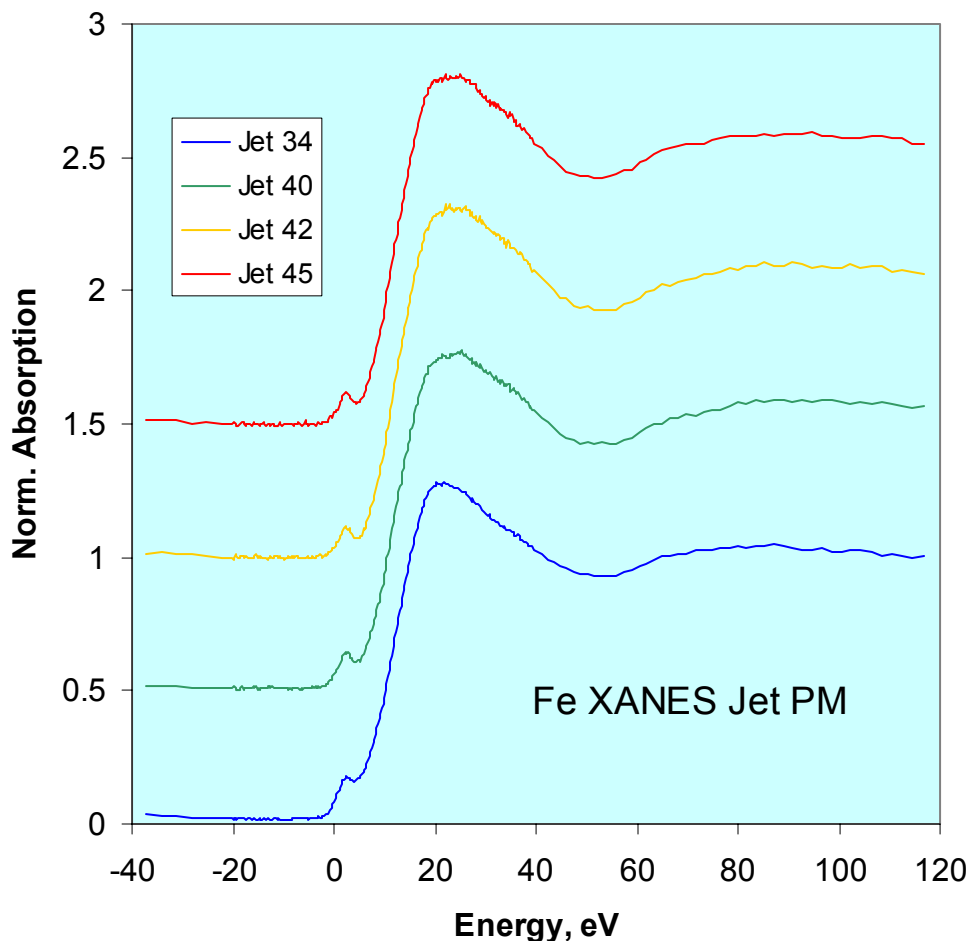


Figure 27. Iron XANES spectra of Jet PM samples from Wright-Patterson AFB.

E. Ambient filter samples.

Relatively little work was done on characterizing elements by XAFS spectroscopy in ambient PM samples during the current year. However, an exception was the work done on two ambient PM samples collected in the Houston area as part of the Houston, Texas, regional PM study. Two ambient PM samples were collected each for four days during November, 2001, and returned to us for analysis in January 2002. One of these samples was examined by XAFS spectroscopy at the following edges: S, V, Cr, Fe, Ni, Zn and As edges. The signal/noise ratio varied greatly for these elements with Fe, Zn and S being strong, Ni and Cr intermediate and V and As being weak. Both Cr and Fe indicated the presence of significant metallic forms; such forms were evident in the RSFs as well as the XANES spectra of these elements. The remainder of the elements were by and large non-metallic in form; Ni and Zn in the form of sulfates, V as V_2O_4 (??), As as arsenate, and S as sulfate(q.v. Figure 28).

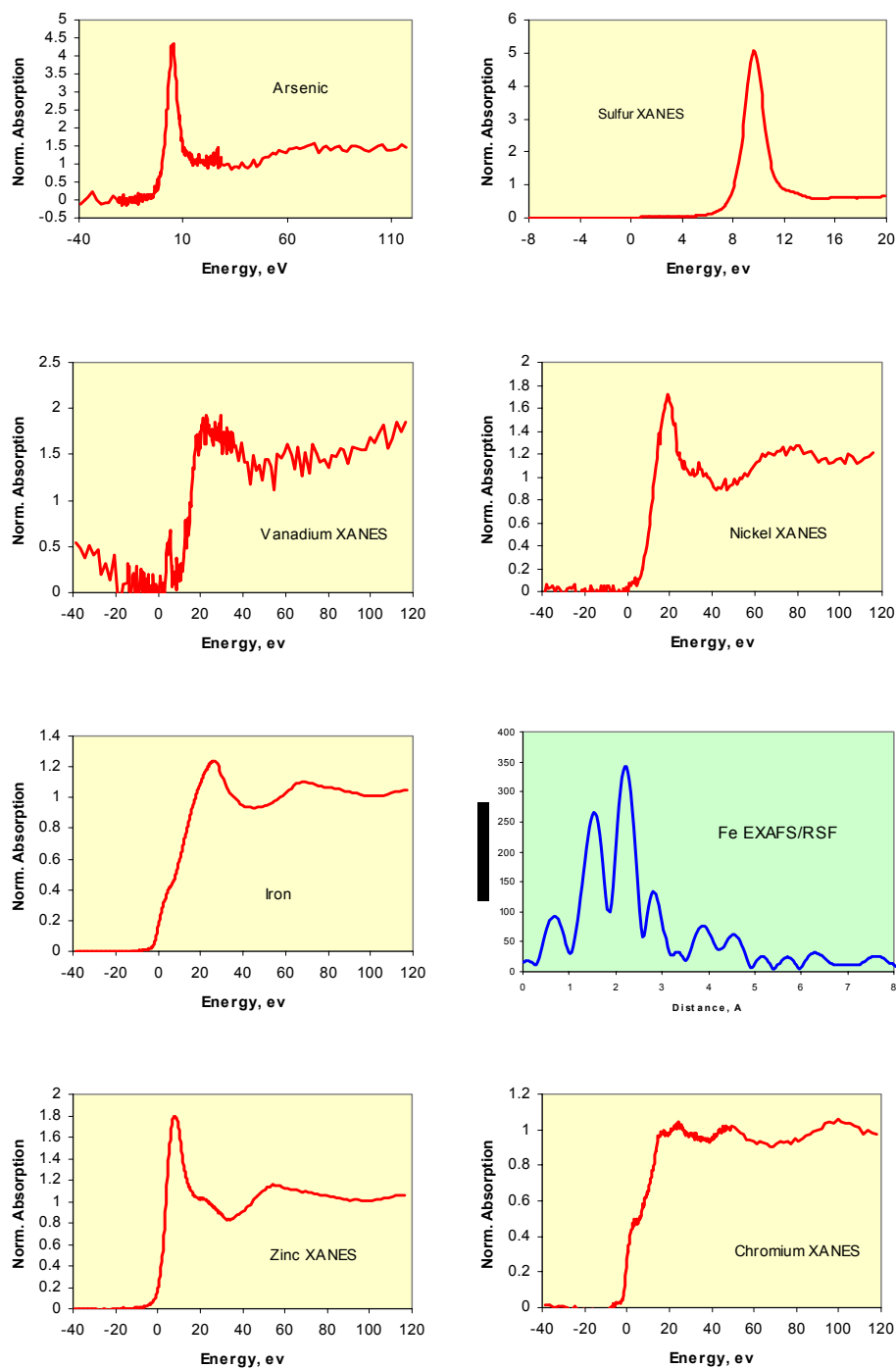


Figure 28: XANES spectra of arsenic, sulfur, vanadium, nickel, iron, zinc and chromium in the ambient filter sample, HRM-3, collected as part of the Houston Regional PM study. Also shown is the Fe EXAFS/RSF plot for iron, proving that the iron is mostly present as metallic iron.

A comparative study was also conducted on a filter sample collected in Lexington for four days. However, only four elements were examined: S, Cr, Ni and Zn. These are shown in Figure 29.

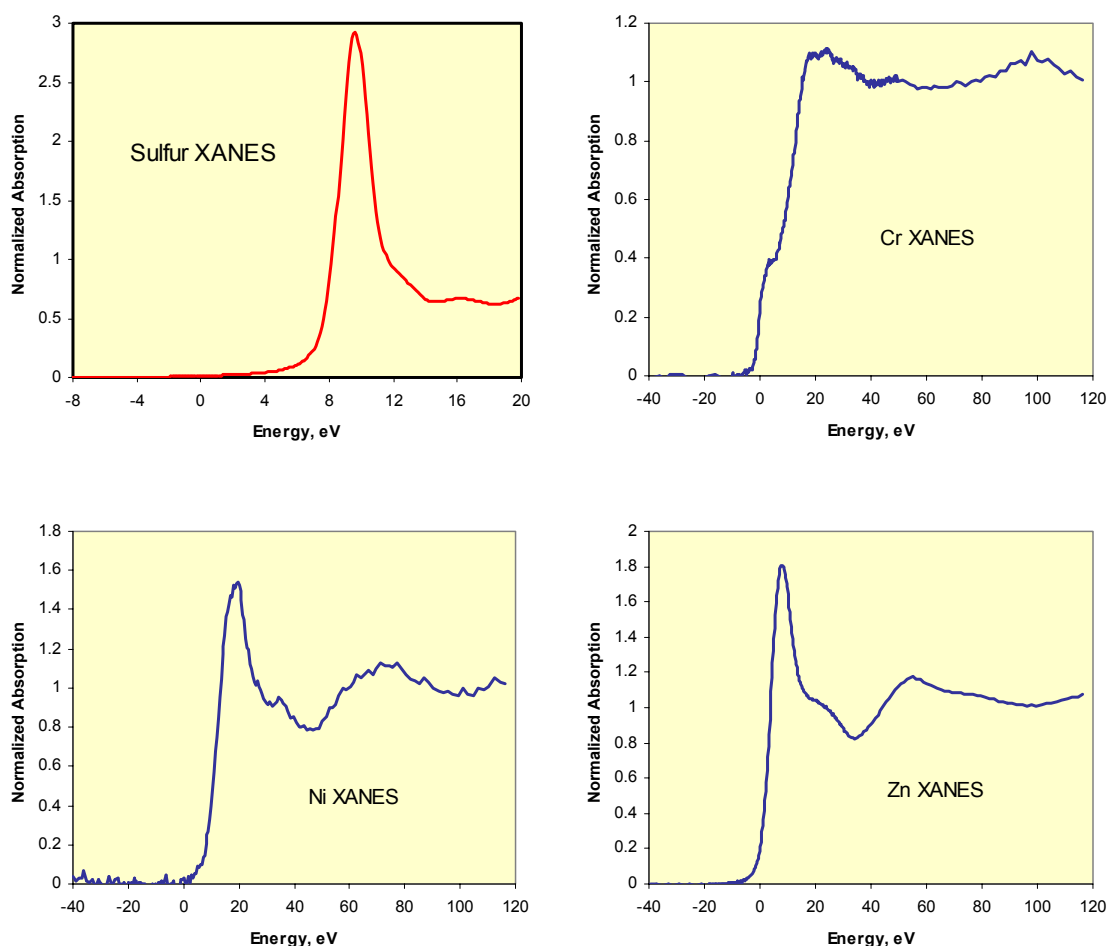


Figure 29: XANES spectra of sulfur, chromium, nickel and zinc in the ambient filter sample, LEX-58, collected in Lexington, KY.

In comparison to the data for the Houston sample, the XANES data exhibited for S, Ni and Zn in the Lexington sample are surprisingly similar and suggest that they are present predominantly as sulfates. Chromium in the Lexington filter is partly metallic; the fraction of metallic chromium is less than that present in the Houston sample.

Conclusions

Significant progress has been made in metal speciation of fine particulate matter from combustion sources. The combination of leaching using aqueous or acid solutions with XAFS spectroscopy has revealed a wealth of information about minor phases present in both coal and ROFA PM samples. Such studies have significantly augmented our earlier studies based solely on XAFS examination of the original bulk material. Some conclusions are listed below for the different types of materials investigated.

It has shown quite conclusively that sulfates are the dominant form of occurrence of most metals in ROFA PM and that most metals exhibit minor sulfide and oxide occurrences. The major exceptions to this overall scheme are (i) iron, which appears not to form significant sulfates; and (ii) base metals such as lead and copper, which appear not to form oxides. The sulfide occurrences constitute a higher fraction of the metal in the coarse PM fractions compared to fine PM fractions. In contrast, oxide phases tend to be found only in the finest PM < 2.5 μm fractions. We suspect that these differences relate to the combustion process and that the oxide is formed as burn-out goes closer to completion, whereas sulfide is preserved in coarser particulate.

For coal, the combination of leaching and XAFS spectroscopy is not so revealing as it is for the ROFA-derived PM samples. However, significant differences are brought about for sulfur and arsenic, including the conclusive demonstration of the existence of a minor fraction of the highly toxic oxidation state of As, As(III), in residues of acid-leached samples. For metals, leaching is less effective because they are present as aluminosilicates, aluminosilicate glass, or oxides, none of which are significantly affected by aqueous leaching treatments and only slightly so by acidic (1N HCl) treatments.

An examination of PM from engines burning jet fuel has been initiated. So far only sulfur and Fe have been examined in such materials. Sulfur is present almost exclusively as sulfate, but some very minor organosulfur compounds (thiophene, sulfoxide) have also been identified.

Ambient PM_{2.5} collected on Teflon filters continue to be examined by XAFS spectroscopy. In recent months, we have compared and contrasted the speciation of sulfur and a number of metals collected on PM_{2.5} filters in Houston, TX, and in Lexington, KY. Despite significant differences in the industrial natures of the two cities, some of the metals occur in very similar forms in the two locations. Most interesting was the observation of both iron and chromium present in metallic forms in these two locations.

Immediate future work in this area will concentrate on preparing publications based on the data presented herein and in the previous year's report. A good start has been made on a manuscript describing the results of the combined XAFS and leaching approaches for elucidation of the forms of elements in ROFA PM. In addition we will continue to pursue some new directions. Plans have been made to examine other ROFA PM samples by means of ASAXS measurements at not only the Ni K-edge but also the V K-edge to supplement the study briefly described herein on Ni in the BL5 ROFA samples. We hope also to expand our range of combustion PM samples to include samples from biomass combustion and from wildfires.

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Characterization of fine PM derived from the combustion of coal by CCSEM and fractal analysis

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Introduction

Flyash that is not trapped by pollution control devices can make a significant contribution to the inorganic component of ambient airborne particulate matter (PM). Concerns about environmental and public health effects of fine airborne PM have stimulated research on the characterization of the physical and chemical properties of flyash particles [1-3]. Structural characterization of individual particles as a complement to conventional bulk analysis can provide valuable insight into the origin, formation, transport, reactivity, and environmental impacts of PM. Computer-controlled scanning electron microscopy (CCSEM) is a powerful tool for characterizing the size, morphology, and chemical composition of large numbers of individual particles. Typical applications of CCSEM to the study of flyash and PM can be found in references 3-11.

In this study, CCSEM in combination with manual SEM has been used to characterize the particle size distribution, morphology and chemical compositions of fourteen CFA (Coal Fly Ash) PM samples generated in combustion experiments conducted at the U.S. EPA National Risk Management Research Laboratory (NRMRL) [8]. As discussed in details below, the CCSEM technique is able to provide information on the chemistry, size, and shapes of the CFA PM that appears to be quite useful for source attribution, not only for distinguishing CFA from other types of inorganic PM, but even in distinguishing different sources of CFA.

Experimental Procedure

Sample generation: The samples were prepared in combustion experiments conducted at the EPA's National Risk Management Research Laboratory (NRMRL) in North Carolina using a down-fired, refractory-lined laboratory combustor rated at 50 kW. The samples were generated by combustion of three high-volatile bituminous coals from the eastern U.S., viz., Ohio, Pennsylvania (Pittsburgh #8), and Western Kentucky, and four coals of differing ranks from the western U.S., viz., Utah (bituminous), Wyoming (Powder River Basin, subbituminous), North Dakota (lignite), and Montana (lignite). The fine particles were separated by a cyclone apparatus into fractions with mean diameter $>2.5\ \mu\text{m}$ ($\text{PM}_{2.5+}$) and $<2.5\ \mu\text{m}$ ($\text{PM}_{2.5}$). A more detailed description of the combustion apparatus and sampling procedure, as well as research on the concentrations and molecular structures of potentially toxic trace elements in this suite of samples, are available elsewhere [12, 13].

CCSEM procedure: CCSEM analysis procedures used for flyash in this investigation have been described in detail elsewhere [6-11]. Briefly, the flyash is dispersed onto a polycarbonate filter by sonication in and filtration from high-purity methanol. The amount of material on the filter is adjusted to achieve an optimum density of non-

overlapping particles on the filter. The electron beam is then rastered across the sample in a computer-controlled grid, detecting ash particles on the basis of their secondary electron intensity, measuring a series of diagonal diameters to determine the cross-sectional area of the particle presented to the beam, and determining the approximate composition of the particles from their energy dispersive x-ray (EDX) spectra. Normally, approximately 1200 particles are measured at three different magnifications.

The software used to place the CFA particles into different chemical categories identifies particles in which a single element, two elements, or three elements are dominant and labels them accordingly. Although the resulting compositions can be presented in tabular form, it is more instructive to present the results in the form of graphical ternary phase diagrams, as discussed in more detail in several earlier publications [6-11].

While the CCSEM analysis provides a very informative broad classification procedure for CFA PM, many of the finer particles in the PM_{2.5} size range exhibit a wide variety of complex shapes and boundaries. Therefore, as a new approach to investigate PM_{2.5}, quantitative shape characterization of three CFA samples has been attempted using fractal analysis.

Results and discussion:

Particle size distributions

The particle size distributions (PSD) of the seven PM_{2.5} and the seven PM_{2.5+} fractions from the CFA samples are shown in Figures 1 and 2. Not surprisingly, the PSD based on particle number is much different from that based on particle volume. Particles with mean diameter less than 2.5 µm constitute 80-95% of the total number of particles, whereas particles with mean diameter larger than 2.5 µm constitute 80-95% of the total particle volume and mass. This is true for both the PM_{2.5} and PM_{2.5+} samples.

For western CFA PM_{2.5+} samples (Fig.1), the maxima of the number PSD's lie in either the <1 µm or the 1-2.5 µm size ranges, while those of the volume PSD's lie in the 10-20 µm or 20-40 µm size ranges. For the western CFA PM_{2.5} samples, the maxima of the number PSD's also lie in either the <1 µm or 1-2.5 µm size ranges, but those of the volume PSD's are drawn back into the 2.5-5.0 µm or 5.0-10 µm size ranges. The PRB (Powder River Basin coal from Wyoming) CFA sample shows the narrowest PSD's for both the number and volume size distributions.

Eastern CFA samples (Fig.2) basically show similar trends to the western CFA samples. However, the Pittsburgh #8 samples contain a relatively coarse mode, which is probably due to the contribution of a few big particles. The contribution of big particles to the total volume is of course much greater than that of small particles; for example, the volume of one spherical particle with a diameter of 20 µm equals the total volume of 1,000 spherical particles with diameters of 2 µm.

Major element compositions derived from EDX spectra

Major inorganic element compositions of the 14 CFA PM samples were examined by EDX bulk analysis of pellets prepared from the ash samples. The system software performed an approximate PROZA (A mathematic procedure developed by Bastin et al.) correction on the EDX spectrum and converted the x-ray counts into weight percentage. Table 1 lists the results in the oxide form.

Si and Al are the most abundant elements in the 14 CFA samples, followed by Ca, Fe, and S. Ca is the dominant basic element for the western CFA samples, but significant amounts of Na and Mg are also present. The eastern CFA samples are rich in Fe, but also contain several percent of K and Ca. A significant amount of Ca and S are present in the Pittsburgh #8 CFA samples. The relatively high contents of S in Pittsburgh #8 samples could be related to the combustion condition, since these samples exhibit a black color indicating the presence of partially combusted products.

Typical SEM images and EDX spectra of individual particles

Typical SEM images and EDX spectra are shown in Figures 3 and 4. Glass particles are derived from solidified molten slag are shown in Figure 3. These particles are typically spherical or rounded and are usually derived from the interaction of two or more inorganic mineral phases in the coal during combustion. The spherical Ca aluminosilicate glass particle shown in Figure 3a is primarily the result of the reaction of CaO formed from carboxyl-bound Ca with kaolinite [6, 8], a clay mineral, but it also contains some Mg and Na. The glassy particle in Figure 3 b is probably derived from the reaction of Fe oxide derived from pyrite with clay minerals and quartz. The glass particle in Figure 3c appears to be produced by the melting of a single mineral particle, illite, a K-containing clay [6, 10].

The particles shown in Figure 4 are typical of the non-glass particles commonly observed in CFA. Figure 4a shows a cenospherical Fe oxide particle produced by the high temperature transformations of pyrite [14], Figure 4b shows a rod-like Ca-S particle, which is probably an anhydrite (CaSO_4) crystal, and Figure 4c an irregular shaped aluminosilicate particle with an Al to Si ratio of ~1:1, indicating that it is derived primarily from the clay mineral kaolinite.

Chemical classification of particles

Each particle is classified into a chemical category based on the percentages of the three most abundant elements detected in the EDX spectrum. Since the CFA PM samples are predominantly inorganic, typically containing <5-10% of unburned carbon, the C and O peaks in the EDX spectra were ignored. Only the elements Na through Fe were detected in significant amounts and included in the classification scheme, which is the approach normally used in CCSEM analysis of coal flyash [6-11]. The software classifies particles on the basis of their EDX spectra into single-element, two-element, three-element, and "other" categories. Single element categories are those particles that contain >90% of one element, two element categories those that contain > 80% of any two elements with no third element >6%, and three element categories those for which three elements contribute >80% to the EDX spectrum, with none of the three elements falling below 6%

and no fourth element exceeding 6%. All particles not meeting any of these criteria are placed in the “other” category. The cutoff percentages are selected by the user and it is sometimes instructive to adjust them and observe the effect on the resulting classification results.

Table 2 lists the volume percentage of each category of fourteen CFA PM_{2.5} and PM_{2.5+} samples. All of the samples contain a significant amount of Si-rich particles (quartz), while Fe-rich particles (Fe oxides derived from pyrite) are observed at >1% abundance in all eastern CFA PM samples but in only one western sample. Si-Al particles are the most abundant two-element (not including oxygen) category and are significant in most of the samples. The glassy particles are represented by the three-element categories. For the western CFA PM samples, Ca-Si-Al is the dominant three-element phase, followed by Na-Si-Al. These represent glassy particles formed by the reaction of Ca and Na, which are present in the low-rank western coals as carboxyl-bound molecular species, with kaolinite and, to a lesser extent, with quartz. The glass particles in the eastern samples are derived from two sources: the reaction of Fe oxides derived from pyrite with illite, kaolinite, and quartz; and the melting of illite, a K- and Fe- containing clay. These particle formation processes have been discussed in detail elsewhere [15, 16].

Volume percentage ternary diagrams

Graphical representation of CCSEM data provides a way to reveal some important trends that are obscured in conventional tabular data presentations. In this section, volume percentage-ternary diagrams, in which the atomic percentages are based on EDX spectra normalized to only three elements, are presented for the most abundant three-element categories. The resulting CCSEM phase diagrams are then compared to standard reference phase diagrams [17].

The Ca-Si-Al CCSEM phase diagrams for western CFA PM and eastern CFA PM are shown in Figures 5 and 6, respectively. As noted above, the Ca-aluminosilicate particles in western CFA from low-rank coals are derived primarily from combustion reactions between abundant ultrafine CaO particulates (fume) and the clay mineral kaolinite, which has a Si:Al ratio of 1:1. For eastern CFA from bituminous coals and for the Utah bituminous CFA, however, the Ca-aluminosilicates result from the reaction of a smaller amount of larger CaO particles formed from the mineral calcite with a mixture of the clay minerals kaolinite and illite, which has a composite Si:Al ratio of ~0.8:1. These differences are reflected in the CCSEM phase diagrams. The western/low-rank CFA PM show a fairly broad range of Ca-Si-Al glass particle compositions with Si:Al $\approx$ 1, reflecting abundant, fine particle CaO reacting with kaolinite. The eastern/bituminous CFA PM, on the other hand, exhibit a much smaller Ca-Si-Al composition range with the Si:Al ratio clustered around 0.8. The low Ca Western Kentucky CFA PM shows very little formation of Ca-aluminosilicates. The cluster of vertical bars near the Si apex represents unreacted quartz particles, while the bars falling on the Si-Al boundary represent unreacted aluminosilicates derived from clays.

For the Montana and PRB samples, reference to standard phase diagrams [17] indicates the formation of gehlenite ($2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$) and anorthite ($\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$). The

PRB PM_{2.5} sample shows a more concentrated distribution in the gehlenite region, consistent with its higher Ca content.

Fe-aluminosilicates are derived primarily from the chemical reactions between aluminosilicates derived from clay minerals and the oxidation products of pyrite (FeS₂). These are the dominant aluminosilicate particles present in the eastern/bituminous CFA PM samples, clearly reflecting the fact that Fe is the dominant basic element in these samples. Fe-aluminosilicates are also significant for the Utah CFA samples, since it is a bituminous coal. The Fe-Si-Al ternary diagrams for these bituminous CFA PM samples are shown in Figure 7. As noted earlier, the Si:Al ratio for these particles falls in the 0.6-0.8 range, reflecting the composition of the clay minerals from which they are derived. Fe oxides appear as a cluster of small bars near the Fe vertex. Not surprisingly, the Fe-rich Western Kentucky samples have the greatest abundance of Fe-aluminosilicates and Fe oxides.

Finally, it is of interest to compare the aluminosilicate phases formed by alkalis in the eastern/bituminous and western/low rank CFA PM samples (Figure 8 and 9). For the eastern samples, K is usually the major alkali and it is contained in the mineral illite. On the basis of earlier results [6-11, 16], it is concluded that illite becomes molten at temperatures above approximately 900 °C, with little change in composition except for further reactions with Fe oxides. Consequently, the K-Si-Al ternary diagrams for eastern CFA PM samples exhibit a peak in region appropriate for the composition of the mineral illite. In the case of western/low rank CFA PM, however, a reaction must occur between volatile Na species and kaolinite, leading to the formation of a molten phase that condenses to form a phase called nepheline (NaAlSiO₄). Some volume percentage bars near this composition in the Na-Si-Al diagrams for the western samples were observed.

It is evident that these volume percentage-ternary diagrams derived from CCSEM data on CFA PM are highly characteristic of the mineralogy of the coals that were combusted to produce them. They should therefore be quite useful for source attribution.

Quantitative characterization of particle shapes by fractal analysis

The concept of fractal dimension was first introduced by Benoit Mandelbrot in 1967 and more specifically in 1977 [18]. Fractal analysis has become a very important field of modern mathematics. Fractal dimension is a new parameter used to describe the irregularity of shapes at different magnifications. The primary aim of the fractal analysis is to distinguish shapes or curves with complicated contours, which normally cannot be described by traditional geometrical or topological approaches. Previous applications of fractal dimension to aerosol studies have been reported [20-22]. In this study, SEM images of ash particles have been used to calculate their two-dimensional boundary fractal dimensions.

Fractal dimension is related to the measuring scale range. Based on the fractal dimension value at a certain range of measuring scale, three fractal dimensions have been used, i.e., Overall dimensions (FD_o), textural dimensions (FD_t) and structural dimensions (FD_s). Textural dimensions and structural dimensions are related to the textural and structural

characteristics of the particle shapes, whereas the overall dimension can be considered as an average value of the former two. Fig. 10 shows the SEM images of two particles (Montana CFA PM_{2.5}) and their overall fractal dimensions. The spherical particle on the top has a fractal dimension of nearly 1, while the irregular particle below has a fractal dimension larger than 1. A perfect circle has a fractal dimension of 1.0. With increasing complexity of the particle shapes, the value will approach 2.0.

An example of textural dimensions and structural dimensions is shown in Fig. 11. The carbonaceous particle in Figure 11a has a textural dimension of 1.08, while the agglomerated soot particle of Figure 11b has a smaller value of 1.06, due to the spherical characteristics of its primary particles. The value of the structural dimension of the agglomerated soot particle (Fig. 11a), however, is much more than that of lower carbonaceous particle (Fig. 11b), because of its irregular chain-like structure.

Fig.12 compares the fractal dimensions of some carbonaceous particles found in Western Kentucky and Pittsburgh #8 PM_{2.5} samples. The fractal dimension increases with the increasing complexity of particle shapes. Carbonaceous particles of West Kentucky sample show irregular bulk structures, while those of the Pittsburgh #8 sample exhibit agglomerated chain-like structures. These shape differences can be clearly differentiated by their textural and structural fractal dimensions.

Further evaluations of the value of fractal dimensions as a PM classification parameter are in progress.

Summary and Conclusions

CCSEM and other SEM analyses have been performed on coal flyash (CFA) PM_{2.5} and PM_{2.5+} samples produced by the combustion of four western coals (two subbituminous, one lignite, and one bituminous) and three eastern coals (all bituminous). The results are summarized below.

4. Particle size distributions (PSD) establish that particles with mean diameter < 2.5µm constitute 80-95% of the total number of particles, whereas particles with mean diameter > 2.5µm constitute 80-95% of the total volume for both PM_{2.5} and PM_{2.5+} samples produced from CFA by a cyclone separator. The maxima of the number PSD's lies in either <1 µm or 1-2.5 µm size ranges for both PM_{2.5+} and PM_{2.5} samples, while that of the volume distributions lies in the 10-40 µm size ranges for PM_{2.5+} samples and the 2.5-10 µm size ranges for PM_{2.5} samples.
5. Volume percentage-ternary phase diagrams generated from CCSEM EDX compositional data appear to be useful for source attribution. Western/low rank CFA PM are dominated by Ca-aluminosilicate phases, while eastern/bituminous CFA PM exhibit significant amounts of Fe-aluminosilicates. The resulting ternary Ca-Si-Al and Fe-Si-Al diagrams exhibit distinctive composition ranges and Si:Al ratios.
6. Alkali aluminosilicates also appear useful for source attribution. Na-Si-Al diagrams are distinctive for western/low rank CFA PM, while K-Si-Al provide a fingerprint for eastern/bituminous CFA PM.
7. Fractal analysis may provide a useful new method to quantitatively characterize ash and carbonaceous particles from combustion sources.

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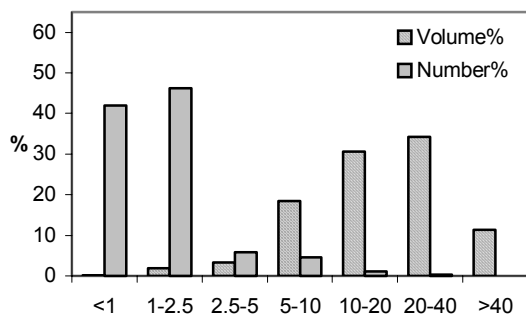
Table 1 Average inorganic compositions of CFA samples based on EDX bulk analysis.
(Normalized to 100 wt%)

Comp. Samp.	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	CaO	TiO ₂	V ₂ O ₅	Fe ₂ O ₃
PRB PM _{2.5+}	1.56	3.83	14.19	39.04	1.70	1.88	0.28	27.65	2.31	0.02	7.55
PRB PM _{2.5}	2.82	4.18	19.40	25.45	3.11	3.94	0.39	30.01	2.82	0.00	7.89
Montana PM _{2.5+}	0.35	4.01	17.67	42.67	0.14	7.03	0.85	21.92	1.60	0.06	3.71
Montana PM _{2.5}	0.40	4.47	19.36	36.00	0.26	5.15	1.29	25.96	2.11	0.00	5.00
N. Dakota PM _{2.5+}	3.87	4.64	10.56	37.41	0.24	4.88	1.55	25.90	1.07	0.08	9.80
N. Dakota PM _{2.5}	1.25	1.66	20.79	52.65	0.66	4.71	1.87	8.60	1.70	0.16	5.95
Utah PM _{2.5+}	0.41	0.99	19.32	62.24	0.40	2.84	1.59	5.87	1.92	0.04	4.37
Utah PM _{2.5}	0.84	1.39	21.49	55.08	0.73	4.33	1.93	7.00	1.98	0.06	5.19
Ohio PM _{2.5+}	0.42	0.48	19.13	51.85	0.69	7.26	2.68	2.13	1.56	0.18	13.63
Ohio PM _{2.5}	0.60	0.61	22.07	52.50	0.81	6.57	3.02	2.26	2.01	0.14	9.41
Pitt#8 PM _{2.5+}	1.09	1.01	15.73	37.95	0.14	11.56	1.38	14.47	1.75	0.00	14.94
Pitt#8 PM _{2.5}	1.22	1.04	20.42	42.58	0.53	10.11	1.91	9.75	1.62	0.03	10.79
WestKY PM _{2.5+}	0.24	0.41	18.45	49.55	0.00	3.07	2.78	0.67	1.34	0.13	23.37
WestKY PM _{2.5}	0.25	0.49	18.78	44.72	0.04	5.14	3.02	1.06	1.80	0.16	24.53

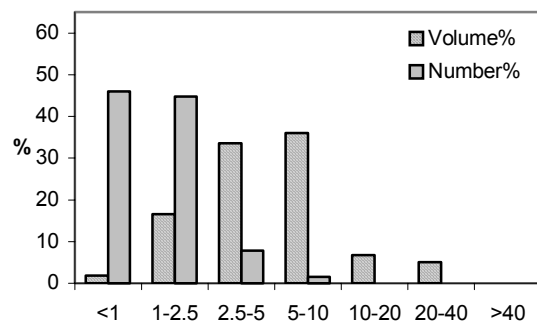
Table 2 Major particle categories and their volume percentage of fourteen CFA samples

	Western coal fly ashes								Eastern coal fly ashes					
	Montana PM _{2.5+}	Montana PM _{2.5}	N.Dakota PM _{2.5+}	N.Dakota PM _{2.5}	PRB PM _{2.5+}	PRB PM _{2.5}	Utah PM _{2.5+}	Utah PM _{2.5}	Ohio PM _{2.5+}	Ohio PM _{2.5}	Pitsb.#8 PM _{2.5+}	Pitsb.#8 PM _{2.5}	WestKY PM _{2.5+}	WestKY PM _{2.5}
Si	8.3	7.8	7.7	17.5	15.9	3.7	11.9	13.1	11.1	11.2	9.9	5.1	6.3	11.4
Ca	3.1	-	3.5	1.3	-	-	2.1	-	-	-	1.9	-	-	-
Fe	-	-	-	1.8	-	-	-	-	5.2	1.1	8.8	1.1	3.4	3.0
Si-Al	10.6	7.1	-	32.1	-	-	55.0	38.4	43.6	32.5	27.3	33.3	23.5	13.3
Si-Ca	4.1	-	2.1	-	1.4	-	-	-	-	-	-	-	-	-
Na-Si-Al	-	-	6.4	-	6.2	11.8	-	-	-	-	1.2	2.5	-	-
K-Si-Al	-	2.3	-	3.3	-	-	1.6	2.2	8.9	5.7	3.3	2.5	13.9	6.9
Ca-Si-Al	59.5	59.8	41.6	25.8	37.0	52.6	13.2	23.5	1.7	4.3	3.3	15.9	-	-
Fe-Si-Al	1.1	-	1.5	6.6	-	-	6.9	14.0	11.8	38.9	16.2	22.2	49.5	58.7
Ca-Al-Fe	-	-	2.4	-	9.9	13.1	-	-	-	-	-	-	-	-
Ca-Fe-Si	-	-	17.4	-	1.5	2.5	-	-	-	-	5.1	-	-	-
Ca-Mg-Al	-	1.1	-	-	4.2	-	-	-	-	-	-	-	-	-
Others	13.3	21.9	17.4	11.6	23.9	16.3	9.3	8.8	17.7	6.3	23.0	17.4	3.3	6.7

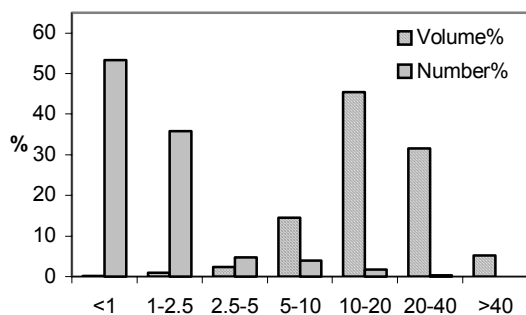
Montana PM_{2.5+}



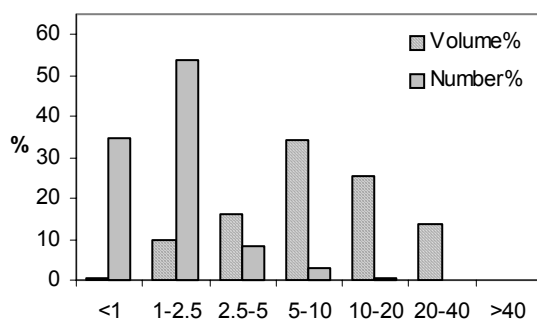
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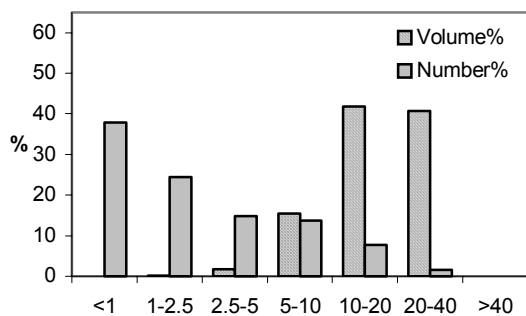
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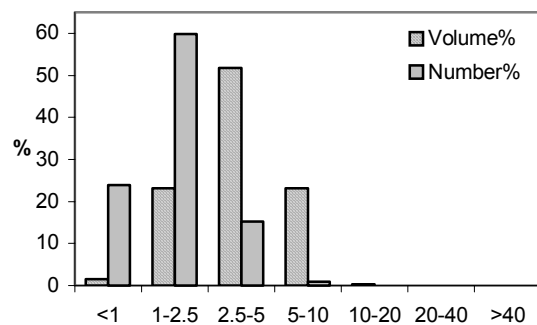
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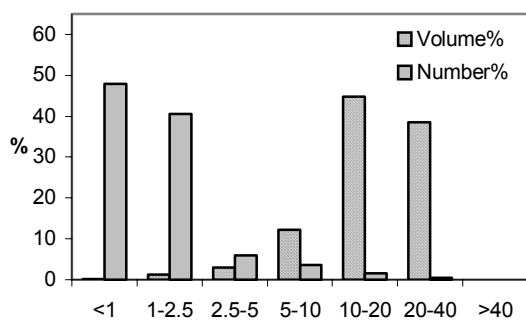
PRB PM_{2.5+}



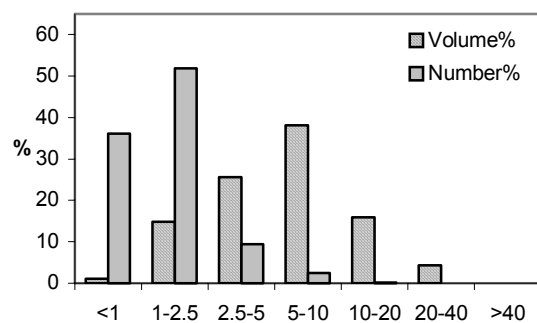
PRB PM_{2.5}



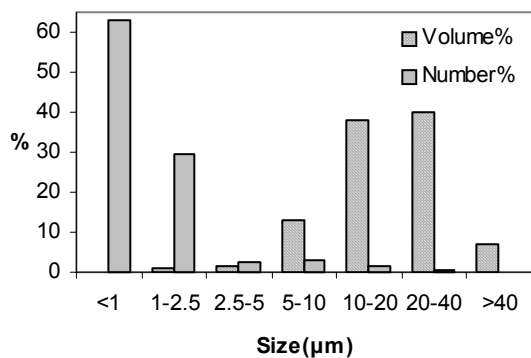
Utah PM_{2.5+}



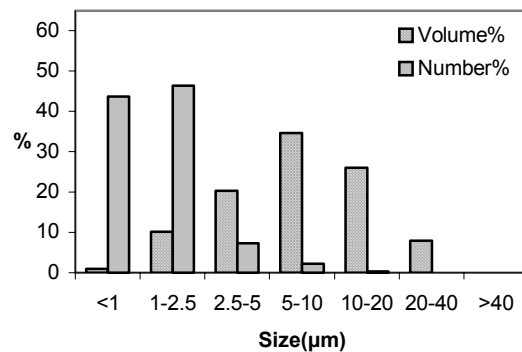
Utah PM_{2.5}



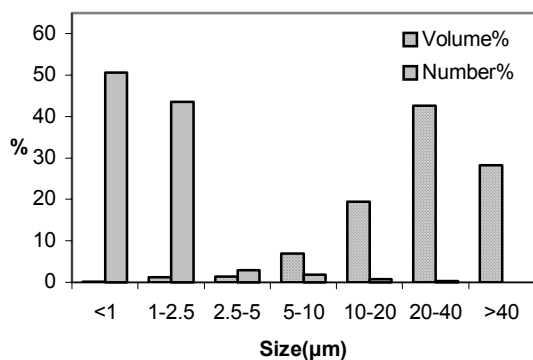
Ohio PM_{2.5+}



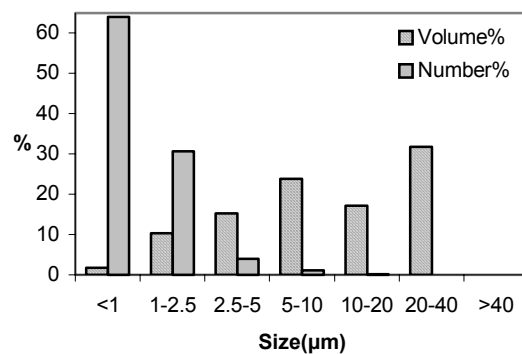
Ohio PM_{2.5}



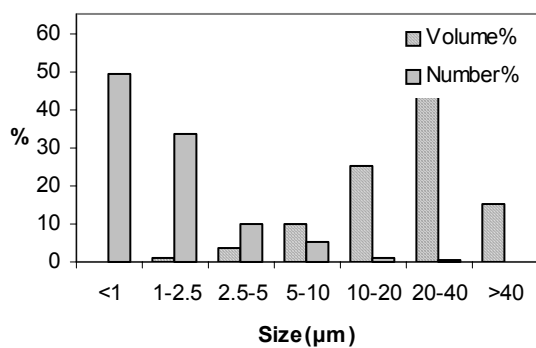
Pittsburgh #8 PM_{2.5+}



Pittsburgh #8 PM_{2.5}



West Kentucky PM_{2.5+}



West Kentucky PM_{2.5}

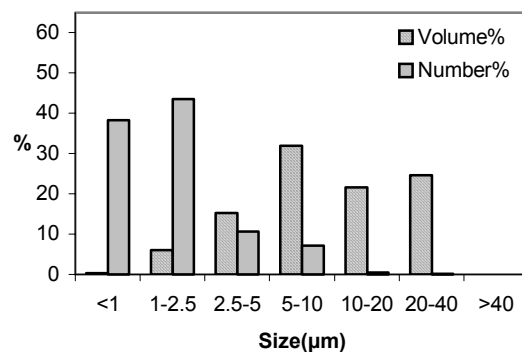
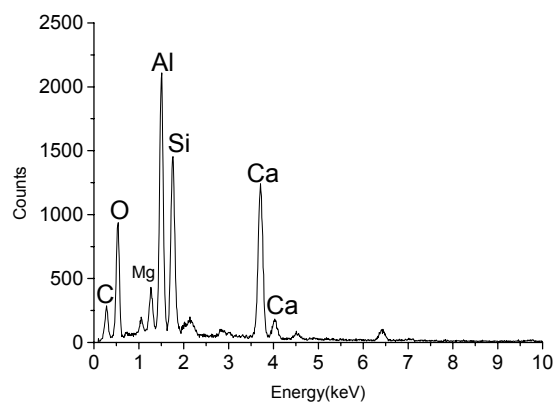
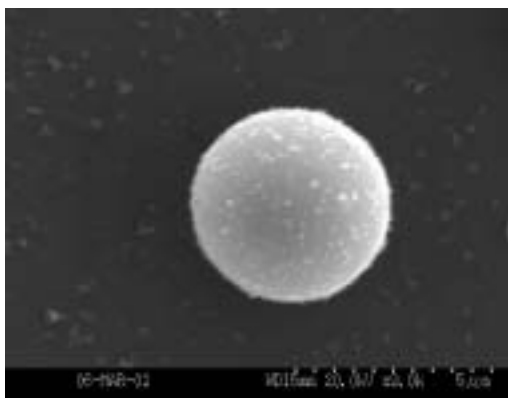
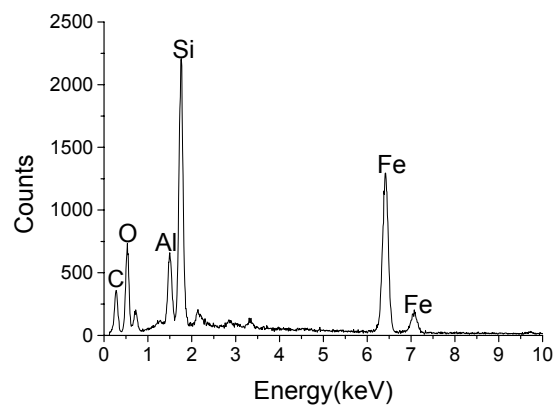
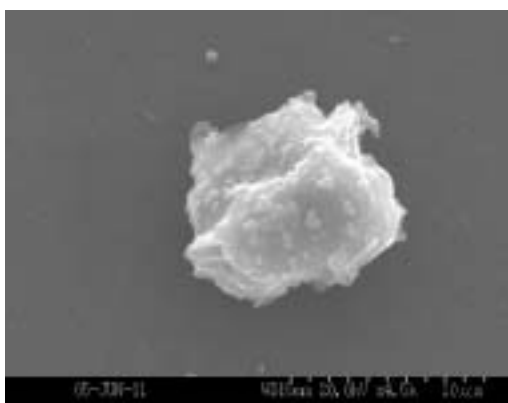


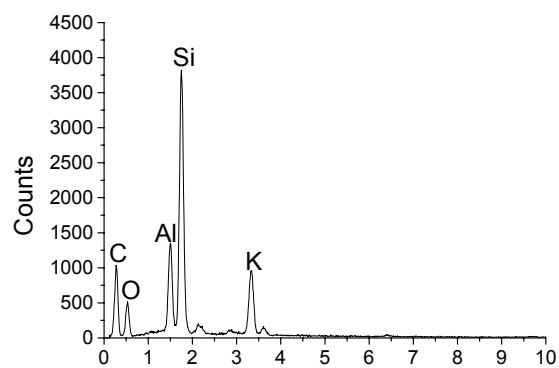
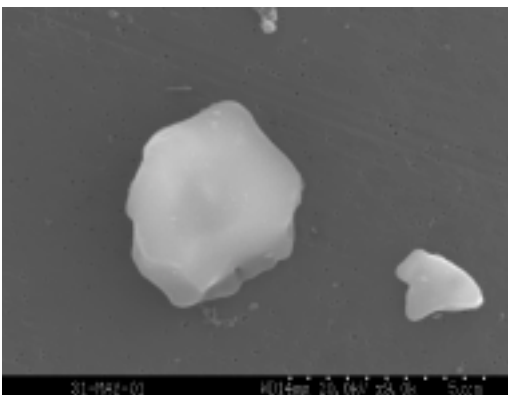
Figure 2 Particle size distributions of eastern CFA PM samples



(a)

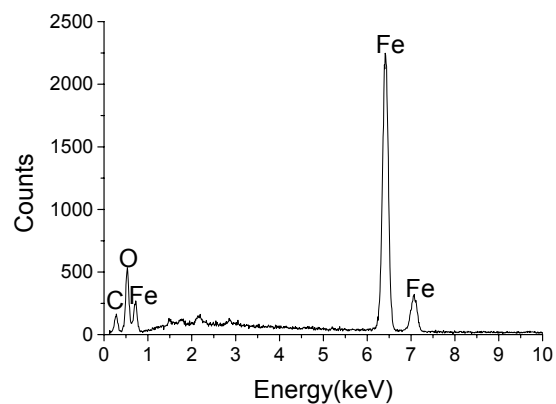
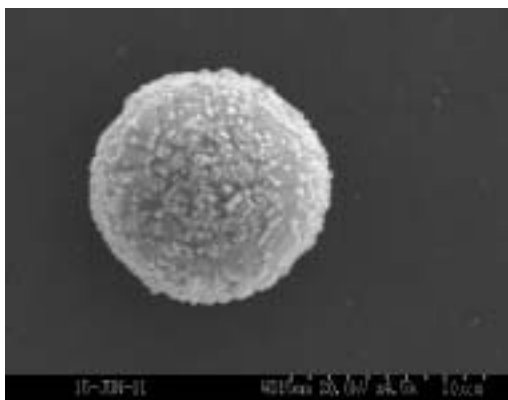


(b)

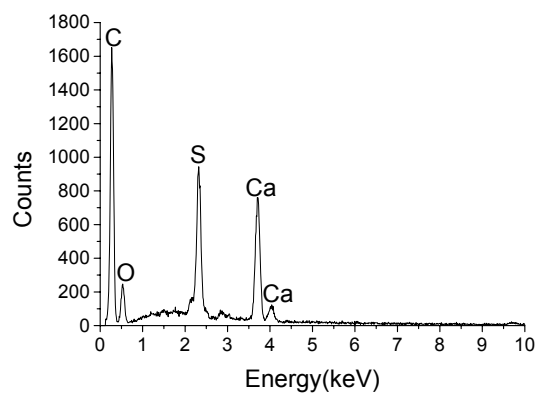


(c)

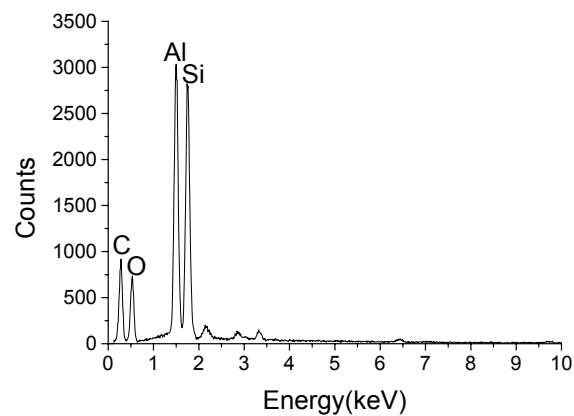
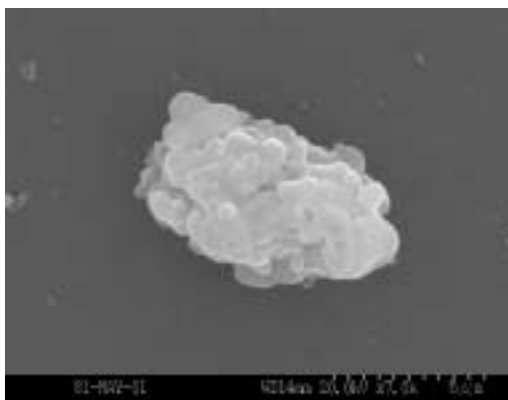
Figure 3 Typical SEM image and EDX spectrum of glass particles. (a) A spherical Ca-aluminosilicate particle. (b) A Fe- aluminosilicate particle. (c) A K- aluminosilicate particle.



(a)

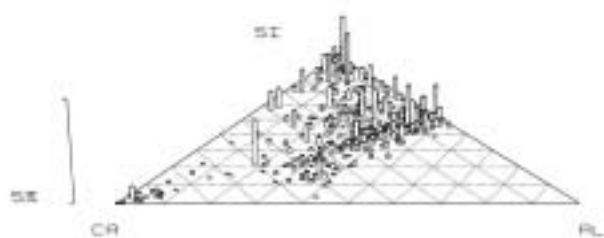


(b)

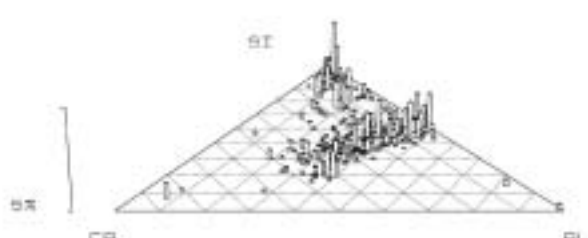


(c)

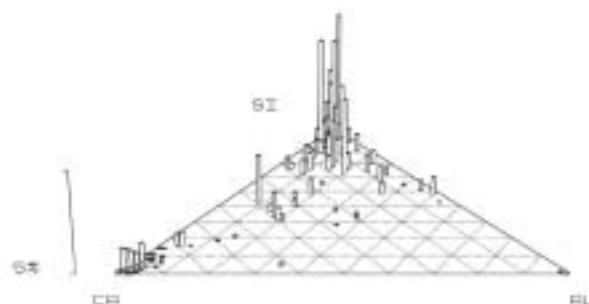
Figure 4 Typical SEM images and EDX spectrums of non-glass Particles. (a). A Fe oxide particle. (b). A rod-like Ca-S particle. (c). An irregular shaped aluminosilicate particle with an Al to Si ratio of 1:1.



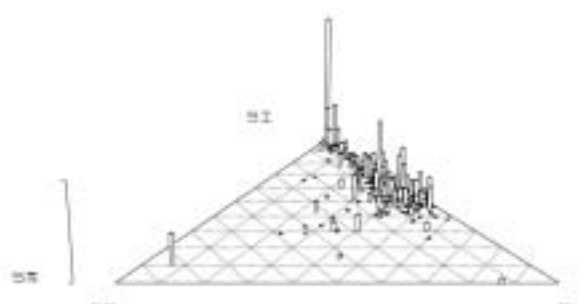
Montana PM_{2.5+}



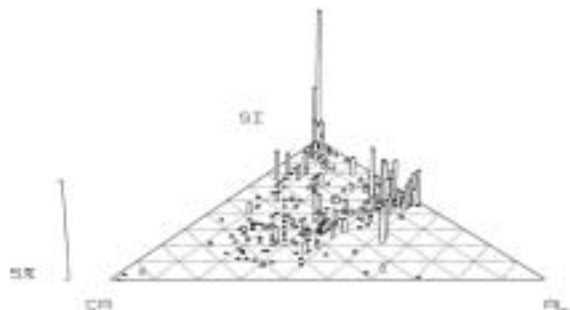
Montana PM_{2.5}



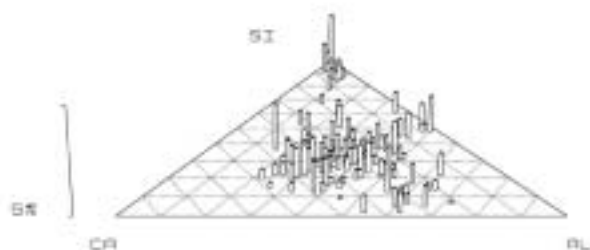
North Dakota PM_{2.5+}



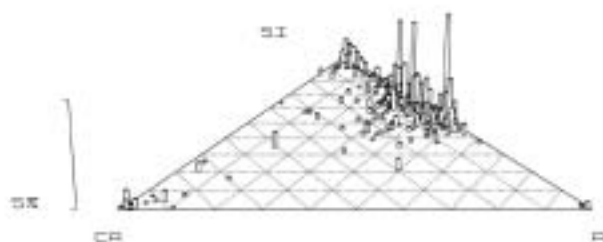
North Dakota PM_{2.5}



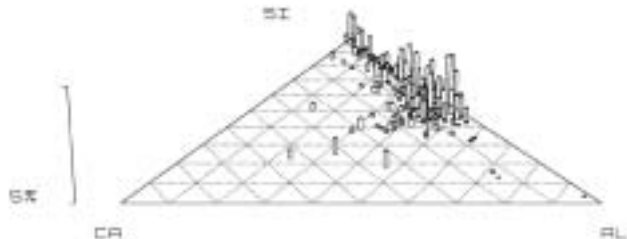
PRB PM_{2.5+}



PRB PM_{2.5}

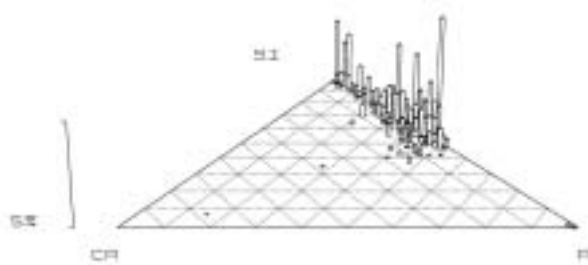


Utah PM_{2.5+}

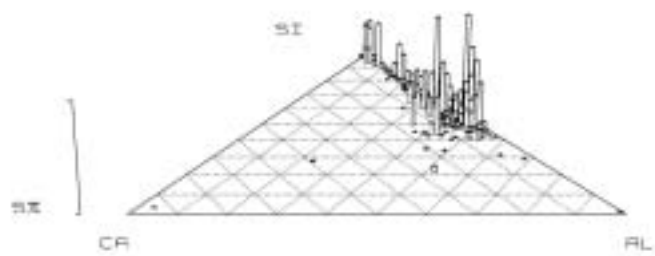


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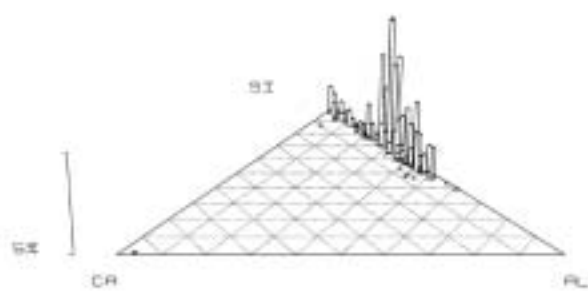
Figure 5 Ca-Si-Al ternary diagrams for western CFA samples.



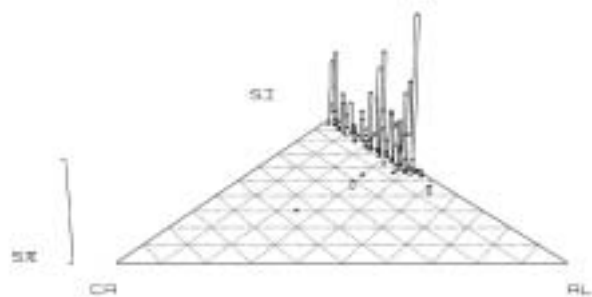
Ohio PM_{2.5+}



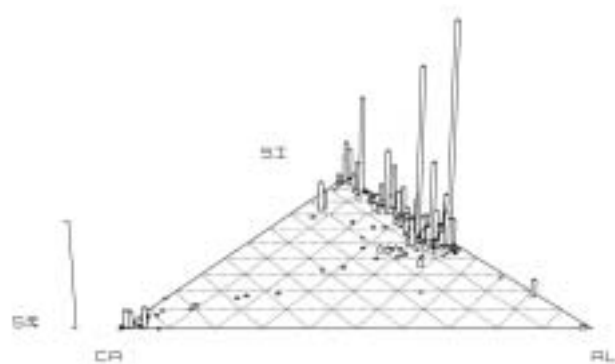
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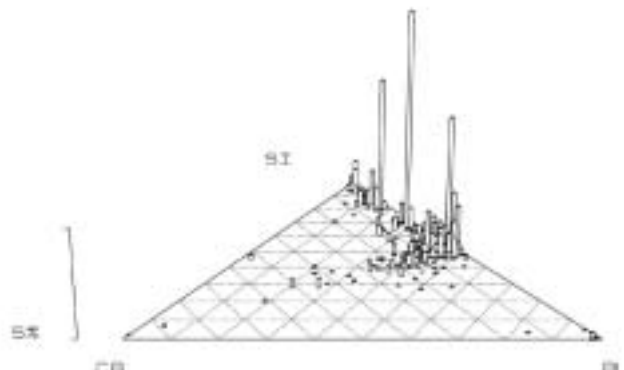
West Kentucky PM_{2.5+}



West Kentucky PM_{2.5}

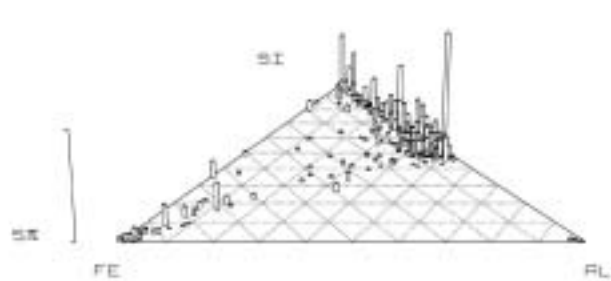


Pittsburgh-#8 PM_{2.5+}

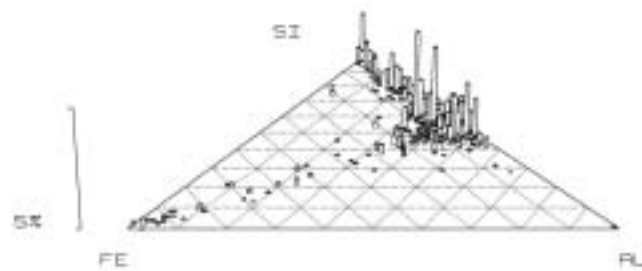


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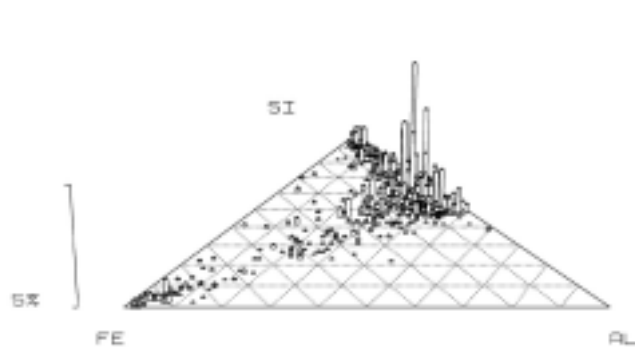
Figure 6 Ca-Si-Al ternary diagrams for eastern CFA samples.



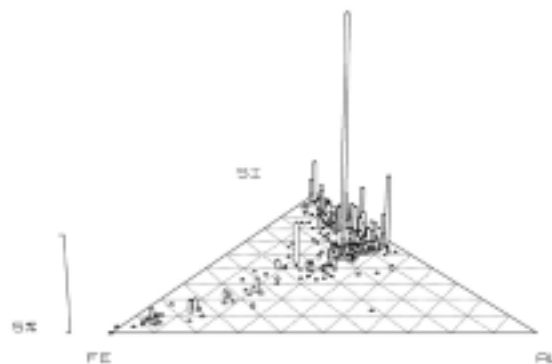
Ohio PM_{2.5+}



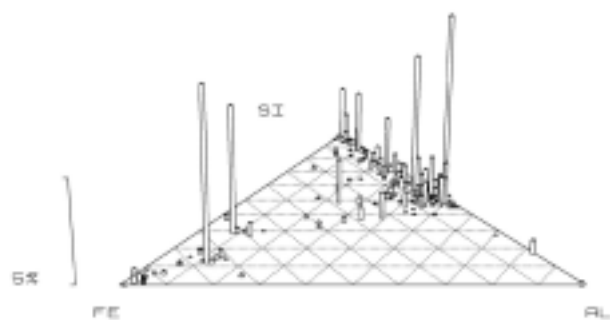
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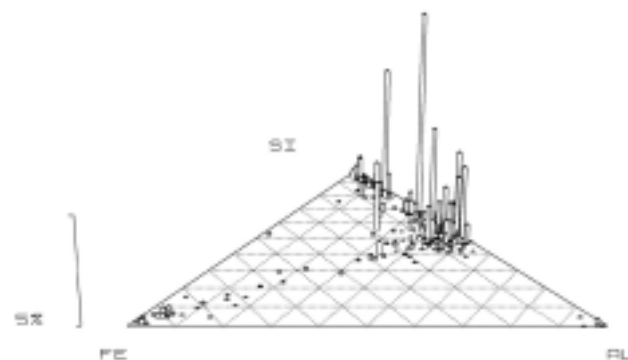
West Kentucky PM_{2.5+}



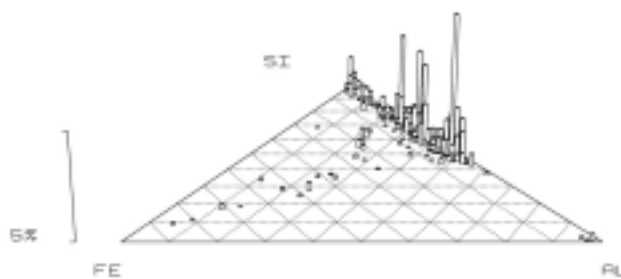
West Kentucky PM_{2.5}



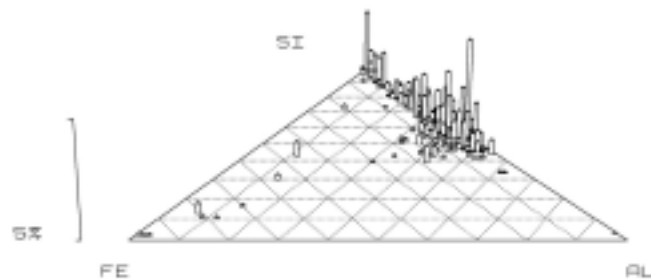
Pittsburgh-#8 PM_{2.5+}



Pittsburgh-#8 PM_{2.5}

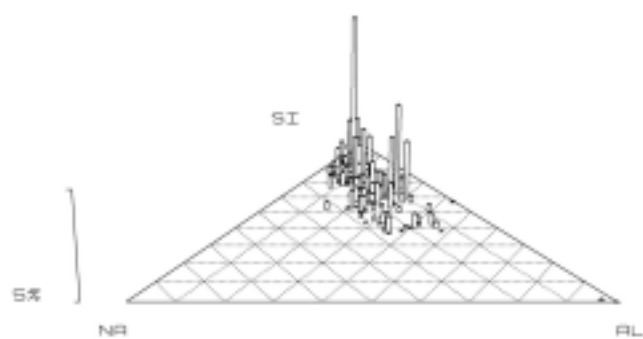


Utah PM_{2.5+}

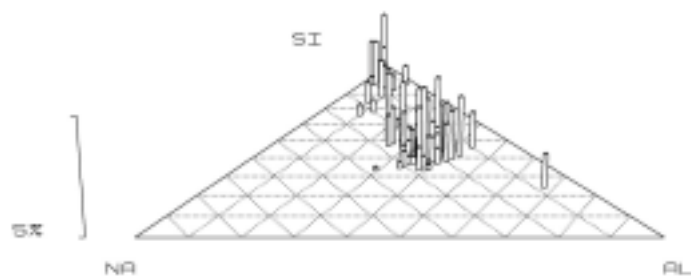


Utah PM_{2.5}

Figure 7 Fe-Si-Al ternary diagrams for eastern and Utah CFA samples.

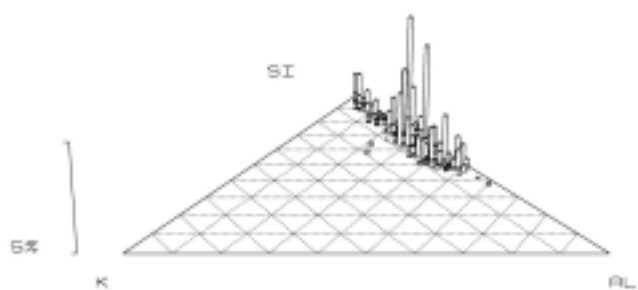


North Dakota PM_{2.5+}

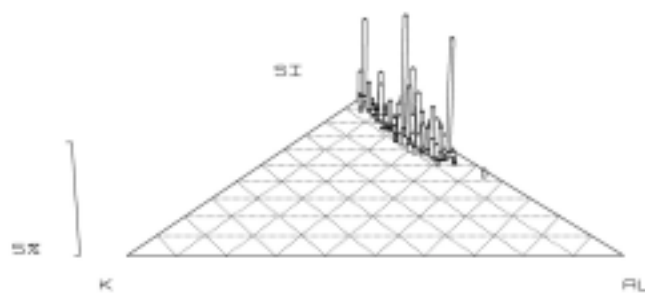


PRB PM_{2.5}

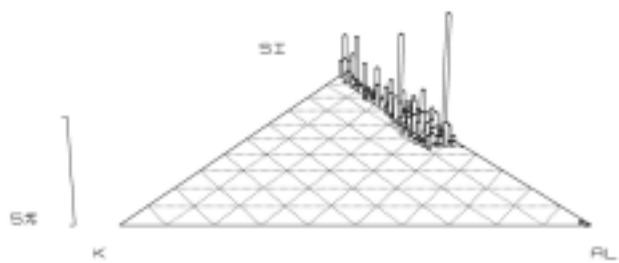
Figure 8 Na-Si-Al ternary diagrams for North Dakota and PRB CFA samples



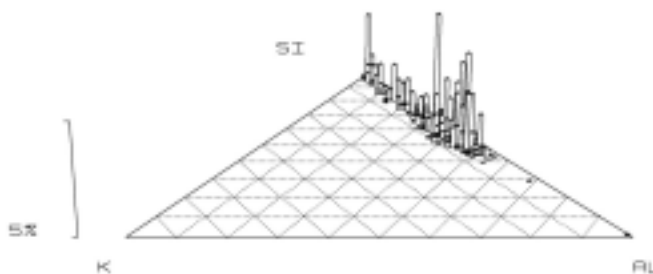
West Kentucky PM_{2.5+}



West Kentucky PM_{2.5}



Ohio PM_{2.5+}



Ohio PM_{2.5}

Figure 9 K-Si-Al ternary diagrams for West Kentucky and Ohio CFA samples

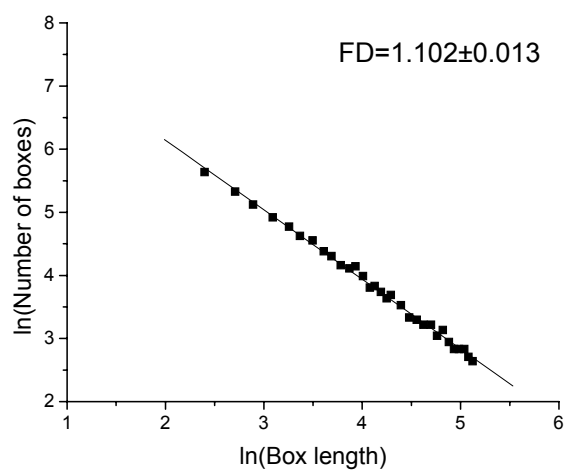
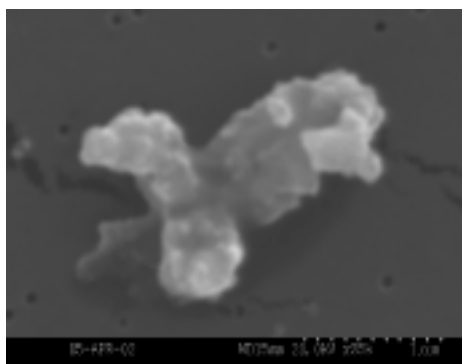
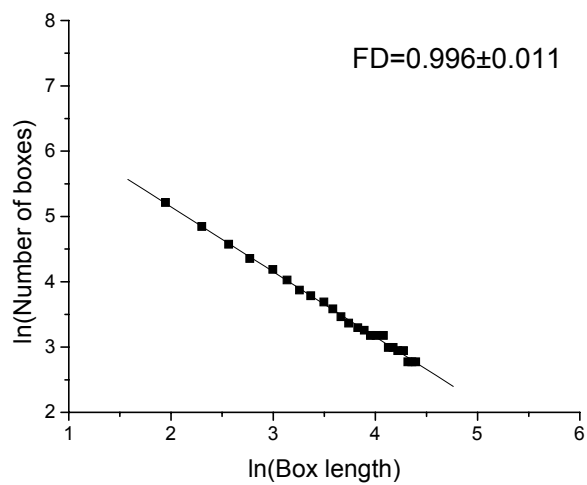
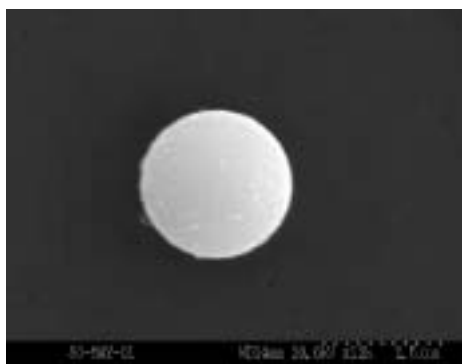
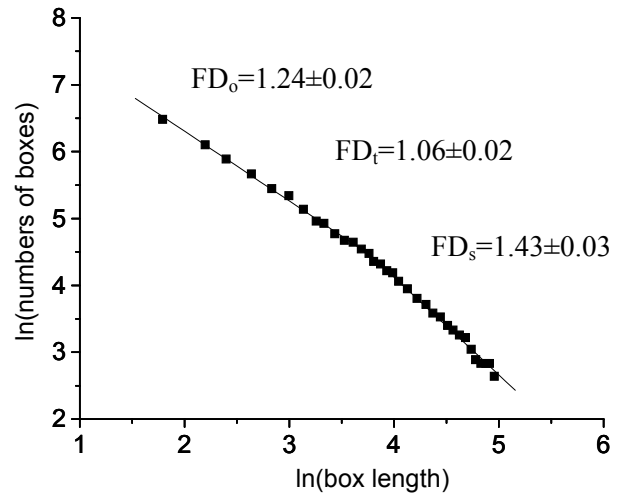
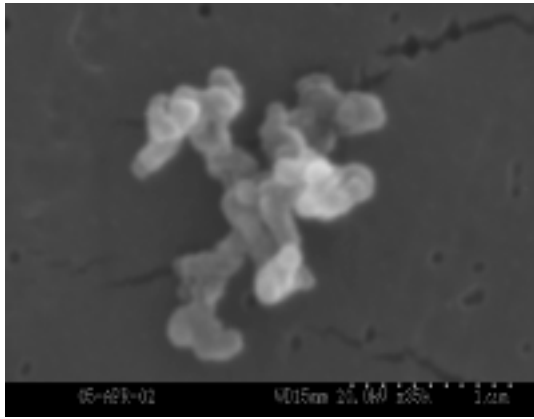
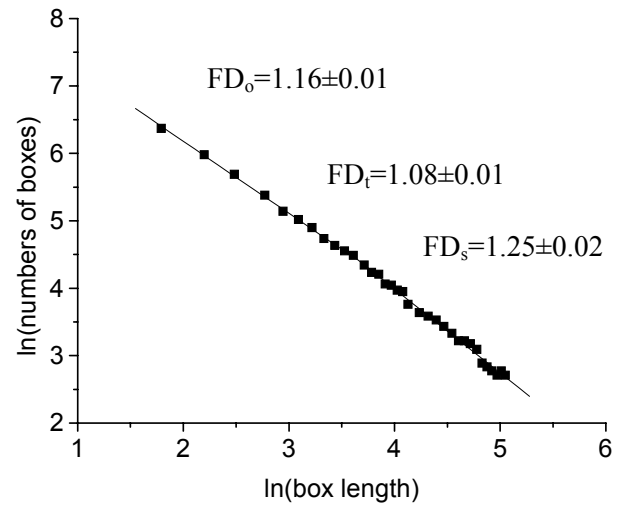
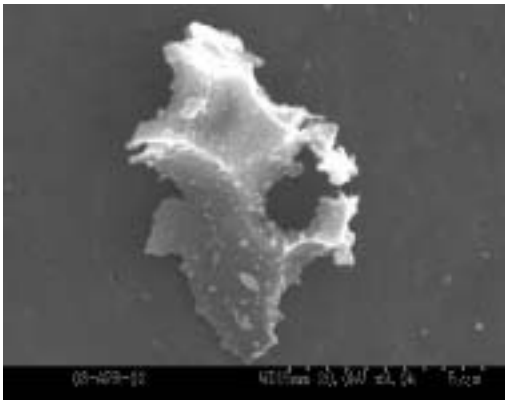


Figure 10 Comparisons of the fractal dimension with different particle shapes.

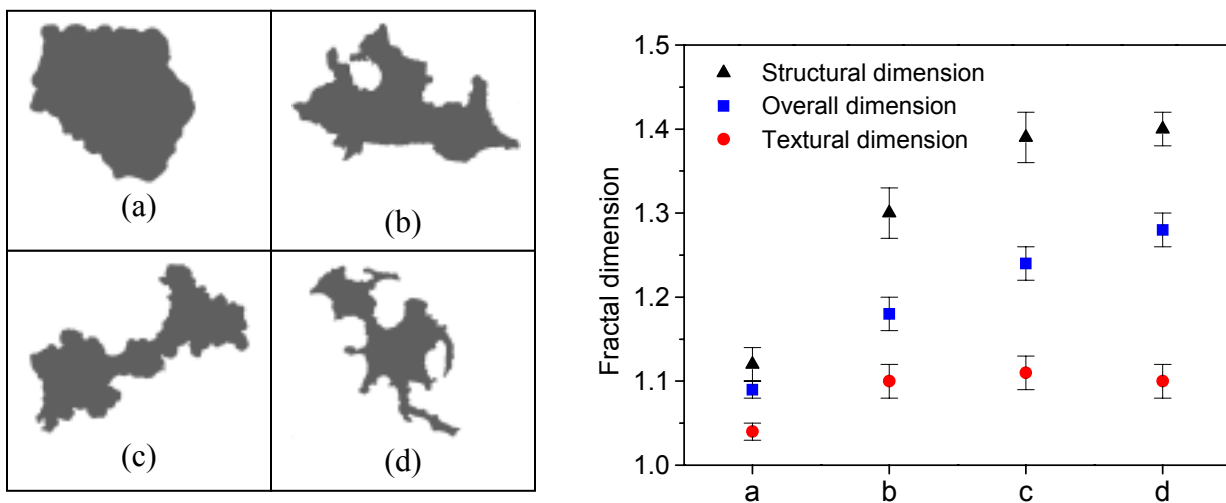


(a)

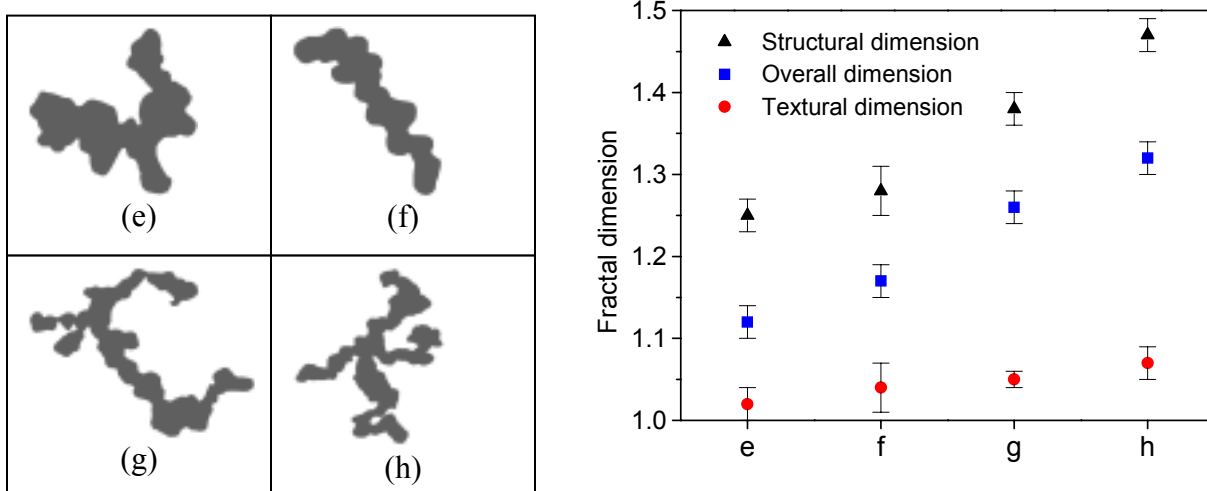


(b)

Figure 11 An example of textural and structural dimensions. (o- overall, t-textural and s-structural)



(I)



(II)

Figure 12. Comparisons of the fractal dimensions of some carbonaceous particles with increased complexity of particle profiles. (I) Irregular shaped particles found in West Kentucky $PM_{2.5}$ sample. (II) Agglomerated soot particles found in Pittsburgh #8 $PM_{2.5}$ sample.

Evaluation of support materials for CCSEM analysis of carbonaceous particles in PM samples

Yuanzhi Chen and Gerald P. Huffman
University of Kentucky

Although CCSEM has had great success in the analysis of inorganic particles, a problem is encountered when attempting to analyze particulate samples for which carbon is a significant constituent. This is obviously the case for airborne particulates, since ambient $PM_{2.5}$ typically contains 20-50% of carbonaceous material. The difficulty is in distinguishing the carbon x-ray signal from the particles from that emitted by the supporting substrate or from contaminants in the SEM sample chamber. In this study, we examined standard spherical glass particles on several substrates to determine the seriousness of this problem and how it could be eliminated.

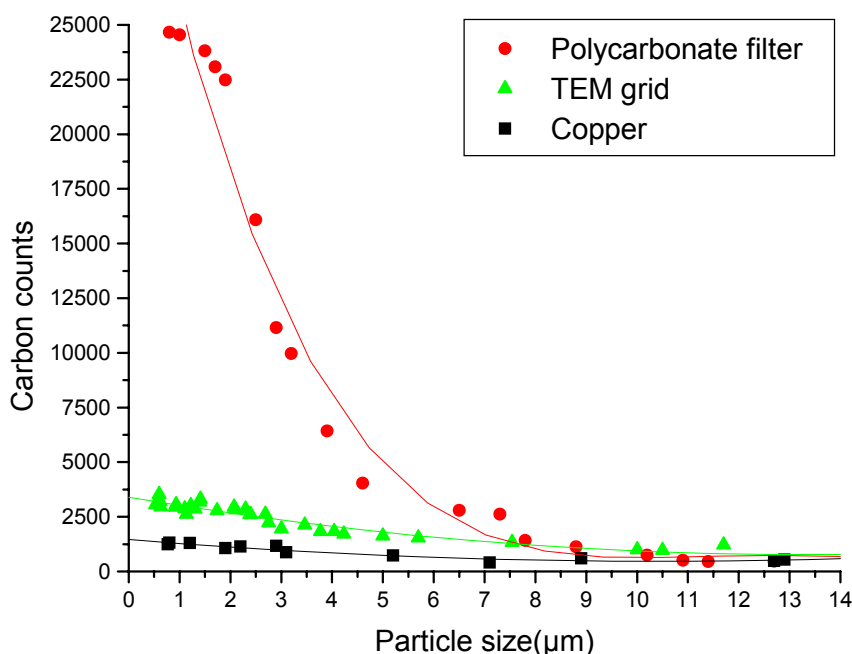
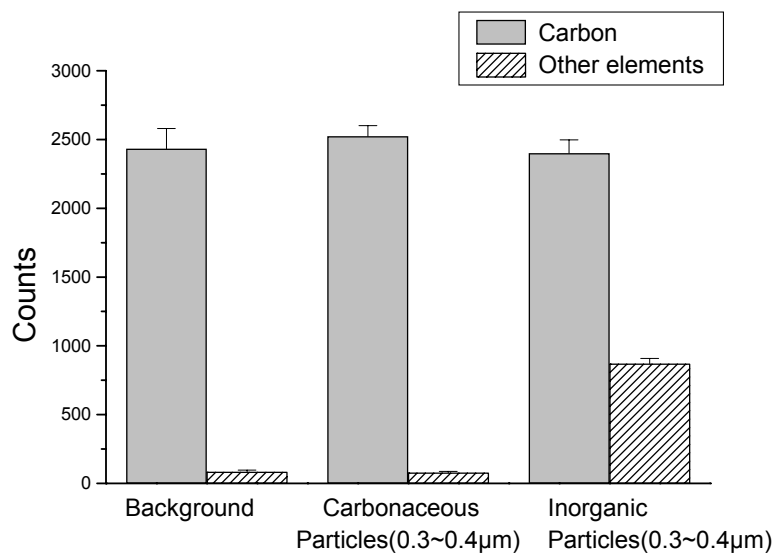


Figure 1. Carbon signal as a function of particle size.

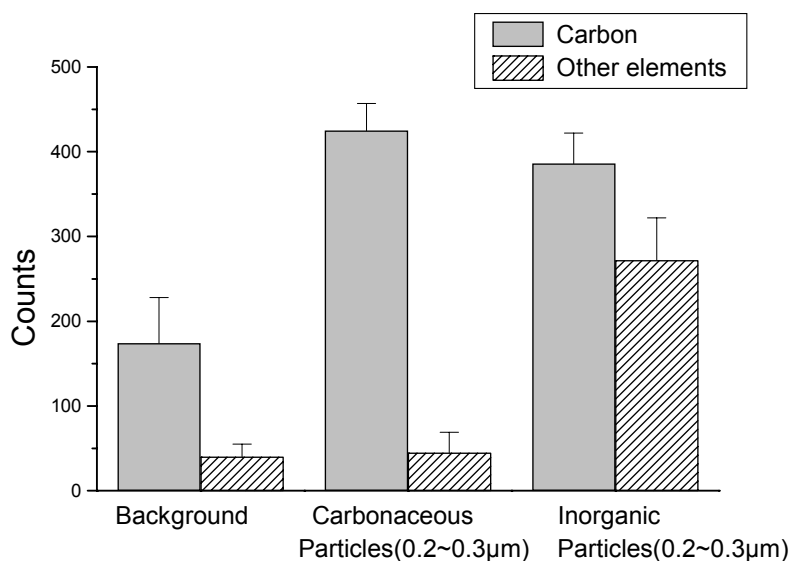
Energy dispersive x-ray (EDX) analysis of K-411 spherical glass particles (Si, Mg, Ca, Fe and O) with different diameters was carried out with the electron beam in the spot mode at an electron energy of 20 keV with an x-ray take-off angle of 35 degrees using several support materials. These included a polycarbonate filter, which is the standard support material used in CCSEM analysis of inorganic particles, a TEM grid, and a polished copper foil.

Carbon signals (total counts) obtained in a 60 sec counting time for these three supports are shown as a function of particle size in Figure 1. The polycarbonate filter shows very strong carbon signals in the small particle size range because it is a relatively thick filter and the electron beam excites carbon x-rays from a region several μm in diameter. The TEM, on the other hand, shows much lower carbon signals because the thickness of carbon film on the grid is in the nanometer range ($\sim 20\text{ nm}$). This was noted previously by Laskin and Cowin in their SEM/EDX study of laboratory-generated aerosols [1]. This indicates that TEM grids can be used as supports for SEM analysis of sub-micron carbonaceous particles. The copper foil substrate shows even weaker carbon signals, which probably arise from chamber contaminants (e.g., hydrocarbons from pump oil). For larger particles ($>7\mu\text{m}$), the difference in the carbon signal is small for all three supports.

The data in Figure 2 were obtained from small ($\sim 0.2\text{--}0.4\text{ }\mu\text{m}$) flyash particles derived from the combustion of a Wyodak subbituminous coal. Figure 2 (a) shows that there is basically no count difference between the polycarbonate filter background and carbonaceous particles. However, inorganic particles are readily distinguished, even though the carbon background counts from the filter are still dominant. Consequently, polycarbonate filters should be used for CCSEM analysis of submicron particles only if they are predominantly inorganic and the carbon background count can be ignored.



(a) Polycarbonate filter



(b) TEM grid

Figure 2. Comparisons of count differences among background, sub-micro carbonaceous and inorganic particles on different support materials.

Figure 2(b) shows the difference between carbon and non-carbon counts among background, carbonaceous, and inorganic particles on TEM grids, which indicates that submicron carbonaceous particles ($\sim 0.2\text{-}0.3\mu\text{m}$) can be distinguished from both inorganic particles of similar size and the carbon film background. TEM grids therefore appear promising as supports for CCSEM analysis of $\text{PM}_{2.5}$ that contains a substantial amount of carbonaceous material. The use of metallic foils, such as copper or beryllium [2], as supports should also be further explored.

Reference:

1. A. Laskin and J.P. Cowin, *Analytical Chemistry*, **73** (2001) 1023-1029.
2. G.P. Huffman, N. Shah, F.E. Huggins, G.S. Casuccio, and W.J. Mershon, *American Chemical Society, Division of Fuel Chemistry Preprints* **36(3)**, 1155-1163 (1991).

Elemental and Isotopic Analysis of PM_{2.5}

J. David Robertson, University of Missouri, Columbia, MO

One of the primary goals of the CRAEMS project is to increase our understanding of the sources and chemistry of fine air particulate from stationary and mobile fossil fuel combustion sources. Key to this effort is the development of additional source signature variables that can be used to identify source emissions. For example, most source-receptor models assign the sulfate observed in ambient particulate to sulfur dioxide produced by coal combustion or emitted from vehicle exhaust. This model may, however, be overestimating the contribution of fossil fuel to the sulfate component of ambient particulate. Another example is the need for marker compounds for assigning particulate to gasoline vehicle emissions. Since lead was removed from gasoline, there has not been an adequate elemental signature for gasoline vehicle emissions and researchers have had to rely upon challenging and lengthy organic compound analysis. And finally, given the large contribution of carbonaceous material to fine air particulate, it is critical that markers be developed for understanding the sources of organic and elemental carbon in PM_{2.5}. Previous studies have relied on organic marker compounds or ratios as indicators for petrogenic or biogenic sources. For example ratios of anthracene and flouranthene are useful for indicating combustion of biological material while the ratio of alkyl PAH's to the parent PAH can indicate fossil fuel combustion. Many of the organic markers used in these studies have, however, multiple sources. Because the identification of reliable marker compounds is critical to our understanding the source and chemistry of PM_{2.5}:

- We have developed a method for determining sulfur isotope ratios and are now investigating the possibility of combining isotope ratio data with trace-element and mode-of-occurrence data to determine what fraction of the sulfate in PM_{2.5} originates from coal combustion versus, for example, combustion of fossil fuels for transportation.
- We have developed analytical methods for measuring the platinum group elements in fine air particulate samples and are working with Environment Canada to investigate how this source signature varies from in-use light duty gasoline motor vehicles.
- We have initiated collaboration with the Center for Accelerator Mass Spectrometry to investigate the use of ¹⁴C as a marker to distinguish between petrogenic and biogenic sources of carbon in PM_{2.5}.

Sulfur Isotope Ratios in PM_{2.5}

Most source-receptor models assign the sulfate observed in ambient particulate to sulfur dioxide produced by coal combustion or emitted from vehicle exhaust. This model may, however, be overestimating the contribution of fossil fuel to the sulfate component of ambient particulate. Hitchcock and Black used sulfur isotope-ratio measurements to identify the source of atmospheric sulfur oxides near Wallops Island, Virginia (¹). In this

anoxic marsh environment there was no evidence of the presence of transported pollutant sulfate even though the sampled air masses had passed over very large sources of anthropogenic sulfur and contained a number of metal pollutants associated with combustion. While one would not expect to see large biogenic contributions to the sulfate in an urban environment, we are investigating the possibility of combining isotope ratio data with trace-element and mode-of-occurrence data to determine what fraction of the sulfate in PM_{2.5} originates from coal combustion versus, for example, combustion of fossil fuels for transportation.

The most important cause for sulfur isotope fractionation in nature is the reduction of sulfate ions by anaerobic bacteria. The extent of fractionation is variable and depends on temperature, the sulfate reservoir, the bacterial metabolic rate, and on the H₂S expulsion rate. Fractionation also occurs during isotope exchange reactions due to the different rates at which sulfur-oxygen bonds are broken. While the $\delta^{34}\text{S}_{\text{CDT}}$ values of petroleum span a wide range from 0.8 to +32 ppt⁽ⁱⁱ⁾, the sulfur isotopic composition of a given pool is constant and pools in the same reservoir rock within a sedimentary basin have similar $\delta^{34}\text{S}$ values. Likewise, the isotopic composition of sulfur in coal varies widely from $\delta^{34}\text{S}$ of +24 to 0.30 ppt. (2)

Natural sources of sulfur in the atmosphere include volcanic gases, sulfur compounds released by sulfate-reducing bacteria, sulfate particles from sea spray, and sulfur compounds released by plants. Anthropogenic sources of sulfur include combustion of coal and fuel oil, petroleum refining, mineral processing, and automobile and truck exhaust. Clearly, one must know the isotope composition of both natural and anthropogenic sources to develop an accurate source apportionment model and many studies have been carried out in Europe, the Arctic, and America to trace sulfate in the atmosphere and in precipitation by using sulfur isotope ratios⁽ⁱⁱⁱ⁾.

Given that inductively coupled plasma mass spectrometry (ICP-MS) is an acceptable method routinely used for the determination of inorganic compounds in ambient air,^(iv) we have developed a method of simultaneously determining the sulfur isotope ratio and inorganic components in a PM_{2.5} sample. The measurements are performed with a VG Axiom high-resolution magnetic sector ICP-MS that is fitted with an alumina injector, HF-resistant microbore PFA nebulizer, and Teflon cyclonic spray chamber. The microbore nebulizer uses a sample flow rate of only 100 $\mu\text{L}/\text{min}$. In order to resolve ³²S and ³⁴S from isobaric interferences, the isotope ratio measurements are made at a mass resolution of 4000. In contrast to many isotope ratio measurements, we are using a single collector. A single run consists of 4 mass sweeps over the ³²S and ³⁴S peaks with 30 points per peak and a dwell time of 20 ms per point. An isotope ratio measurement is the average of 5 repetitions of 10 runs per sample. Each sample measurement is blanketed by a secondary sulfur standard.

Thus far, we have investigated PM_{2.5} from two coal and two fuel oil samples. These were digested using a Milestone Laboratory Systems Ethos Plus sealed vessel microwave digestion system in which 50 mg samples were digested in a 13 ml 8:2:3 high purity reverse aqua regia-HF-H₂O₂ solution. The digested samples were transferred, filtered, and diluted with high purity 2% nitric to a final sulfur concentration of 400 ppb before analysis.

Relative standard deviation values for ³²S/³⁴S of 0.2 to 0.5 % RSD are typical after discarding, at most, one run of the data by selectively removing those values that lie

outside 1 standard deviation of the mean. A precision of 0.2 % RSD will result in an error of 3 ppt on $\delta^{34}\text{S}$ values. While this error is larger than that obtained with a multi-collector thermal ionization mass spectrometry measurement, it is small enough to allow us to distinguish among the wide range of sulfur isotope ratios that one expects from different coal and petroleum sources (+32 to 0.30 ppt).

The sulfur isotope ratio values for the fine particulate matter and fuels from the combustion of two oils and two coals are presented in Table 1. In contrast to our preliminary work first reported during method development, there does not appear to be any fractionation of sulfur isotopes during the combustion/particulate collection of these materials. There also does not appear to be any sulfur fractionation among the different forms of sulfur in Baseline 5 Oil.

Table 1. $\delta^{34}\text{S}$ Values Obtained by HR-ICP-MS

Sample	Fuel	Cyclone	Filter
High Sulfur No. 6 Oil	9.6	10.2	
Baseline 5 Oil		10.7	9.2
Baseline 5 Pentane Residue		10.8	10.3
Baseline 5 Acid Residue		9.5	8.3
Western Kentucky Coal	8.7	6.3	8.5
Montana	-5.7	-3.2	-2.9

Platinum Group Elements in PM_{2.5} from In-Use Gasoline Motor Vehicles

Recently we began collaboration with Lisa Graham of Environment Canada to investigate the occurrence of the platinum group elements (PGEs) found in the fine air particulate from in-use light duty gasoline motor vehicles. This project is an extension of a Natural Resources Canada Program of energy Research and Development (PERD) project entitled “Determination of the concentration, composition and sources of airborne carbonaceous particles in Canada.” The four main components of the original PERD project was (1) Detailed chemical and size distribution measurements to develop complete emissions profiles for the fine particulate matter emitted from current Canadian motor vehicles; (2) Obtaining a complete chemical account of the total PM_{2.5} mass in ambient air by determining the contribution of carbonaceous particles and their main chemical species and classes; (3) Determining what percentage of the carbonaceous particles are from anthropogenic versus natural sources, what percentage of the anthropogenic particles are from transportation and of these what percentage are of secondary and primary origin; and (4) Developing and testing a comprehensive model capable of predicting the mass concentration of particle phase carbon in conjunction with inorganics and other relevant chemical and dynamic processes.

In the PERD study, seventy-five in-use light duty gasoline fuelled passenger cars and trucks were tested on a chassis dynamometer over two repeats of the Hot-505 cycle. For each test, gaseous emissions of CO, CO₂, NO_x and THC were measured. Dilute exhaust concentrations were also recorded second by second over each test. Over the two repeats, samples were collected for determining PM_{2.5} mass emission rate, as well as emissions of SO₂, NH₃, organic acids, organic and inorganic ions, trace metals, organic and inorganic carbon and emissions of a range of organic compounds (alkanes, alkylcyclohexanes, petroleum biomarkers, PAH and PASH). Samples of the engine

lubrication oil were collected from each of the test vehicles to aid in correlating emissions composition with lube oil composition. The vehicles selected for testing were chosen to represent the top 70% of the on-road vehicle fleet in British Columbia. Both vehicles passing their AirCare inspection and vehicles failing the inspection were tested in proportion to their presence in the fleet. The vehicles tested ranged in model years from 1978 to 1998. Of these, 50 were light duty passenger cars and 20 were light duty trucks.

Since lead was removed from gasoline, there has not been an adequate elemental signature for gasoline vehicle emissions and researchers have had to rely upon challenging and lengthy organic compound analysis. As a result of our collaboration with Dr. Graham, we have developed analytical methods for measuring the platinum group elements in fine air particulate samples and are working with Environment Canada to investigate how this source signature varies from in-use light duty gasoline motor vehicles. While all 75 vehicles in the PERD study will be investigated, the results for the first 24, oldest vehicles, are given in Table 2 below.

The samples were prepared by sealed-vessel acid microwave digestion. Optima grade hydrochloric acid (HCl) (6 mL), Optima grade nitric acid (2 mL), and TraceMetal grade hydrofluoric acid (HF) (1 mL) were added to samples. The samples were sealed and digested at 180 C using a mixture of HCl, HNO₃ and HF. After digestion, the samples were cooled to room temperature and the vessels were fitted into an evaporation apparatus and the samples evaporated to near dryness under slight vacuum in the microwave oven. Hydrochloric acid (2 mL) was then added to each sample and the sample re-evaporated. This step was repeated twice more in order to eliminate all HF from the samples. The sample residues were then re-dissolved in 0.24 M HCl, and this solution transferred to preweighed polypropylene test tubes with rinsing. The recovery for the PGEs, from three separate preparations, ranged from 82 – 107%.

While only 24 samples have been analyzed to date, a strong correlation is observed between Rh and Pt in the fine particulate (Figure 1). Likewise, a good correlation is observed between the amount of Pd and Pt (Figure 2) when the limited number of samples are divided into those vehicles designed for the Canadian standard (Figure 3) and those vehicles designed for the U.S. 49 state standard (Figure 4). Given that Zereini *et al.* have recently demonstrated that PGE particles from automotive catalytic converters, particularly those bound to fine particulate matter, are capable of being airborne and transported (^v), these preliminary results indicate that these three PGEs may serve as a strong elemental signature for gasoline vehicle particulate emissions with the improved sensitivities of the high-resolution inductively coupled plasma mass spectrometer. The only other significant source of Pt, Pd, and Rh emissions to the biosphere is the noble metal industry (^{vi}).

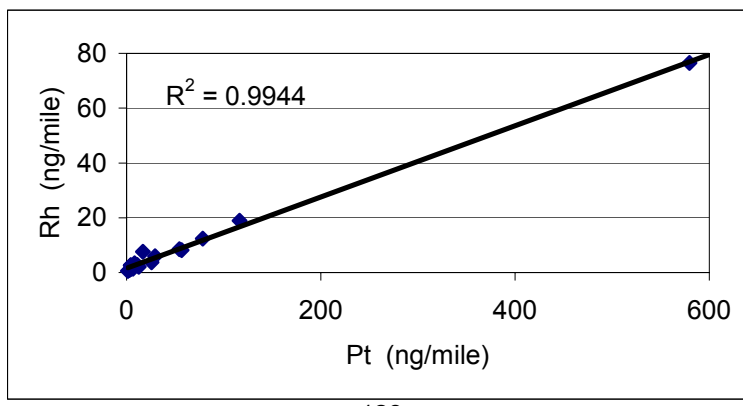


Figure 1. Rh and Pt emissions from Gasoline Vehicles

Table 2. Platinum Group Elements in PM2.5 from Gasoline Motor Vehicles

Year	Make	Model	Category	PM2.5 mg/mile	Rh ng/mile	Pd ng/mile	Pt ng/mile
1978	Pontiac	Acadian	C	9.81	2.49	1.84	7.14
1980	Toyota	Tercel	C	23.26	0.55	(0.89)	1.29
1981	Ford	Fairmont	C	51.23	8.18	(0.21)	56.8
1982	Volkswagen	Jetta	C	39.46	1.43	2.69	6.46
1983	Mazda	GLC	C	53.09	2.66	7.31	4.34
1984	Oldsmobile	Cutlass	C	18.93	(0.045)	(0.18)	1387
1984	Chrysler	LeBaron	C	16.25	2.53	1.25	4.20
1985	Toyota	Tercel	C	99.77	0.89	26.18	2.93
1985	Plymouth	Horizon	C	39.69	8.53	(0.86)	54.26
1986	Mazda	626	C	6.78	12.43	133.74	78.35
1986	Plymouth	Voyager	T	10.55	3.34	3.53	8.18
1987	Toyota	Corolla	C	3.37	(0.05)	11.24	20.68
1987	Toyota	Tercel	C	17.29	(0.13)	329.27	259.40
1984	Buick	Century	C	2.86	(0.05)	74.68	255.44
1985	Toyota	Corolla	C	4.04	6.01	5.47	29.28
1986	Chev	Cavalier	C	13.55	1.58	3.36	5.36
1987	Nissan	Sentra	C	11.79	18.91	30.64	116.25
1987	Pontiac	Fiero	C	14.56	3.75	8.36	25.82
1987	Acura	Integra	C	3.40	(0.10)	(0.75)	72.37
1988	Honda	Accord	C	2.18	1.24	(0.70)	4.31
1988	Ford	Bronco	T	2.98	7.58	7.37	16.83
1988	Chevrolet	Cavalier	C	2.64	2.81	9.57	10.93
1988	Buick	Regal	C	7.00	76.46	(0.21)	579.68
1988	BMW	325	C	9.01	2.13	1.97	12.43

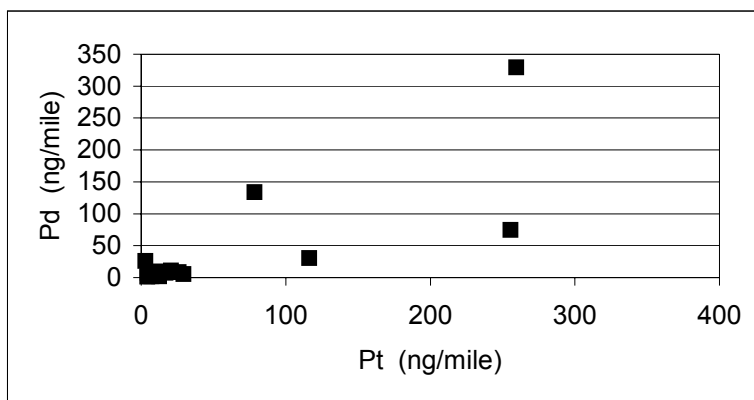
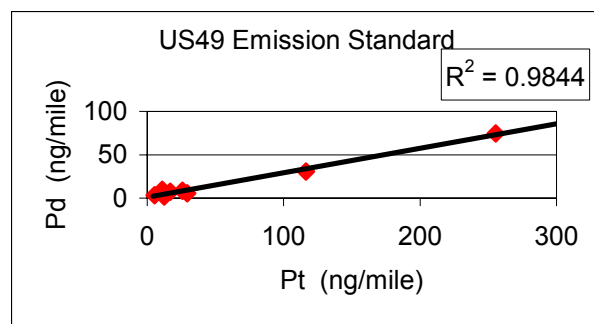
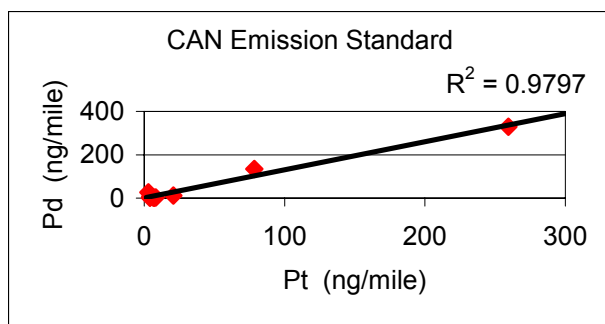


Figure 2. Pd and Pt Emissions from Gasoline Vehicles



ⁱ D.R. Hitchcock and M.S. Black, *Atmosph. Environ.*, 1984, 18, 1.

ⁱⁱ G. Faure, *Principles of Isotope Geology*, 2nd Ed., Wiley & Sons: New York, 1986; pp 526-7.

ⁱⁱⁱ H. Mukai *et al.*, *Environ. Sci. Technol.*, 2001, 35, 1064 and references therein.

^{iv} Compendium Method IO-3.5, Compendium of methods for the determination of inorganic compounds in ambient air, Center for Env. Res. Info. Office of Research and Development, U.S. EPA, Cincinnati, OH.

^v F. Zereini, *et al.*, *Environ. Sci. Technol.*, 2001, 35, 1996.

^{vi} F. Dirksen, F. Zereini, B. Skerstupp and H. Urban in *Emissionen von Platinmetallen – Analytik, Umwelt- und Gesundheitrelevanz*. F. Zereini and F. Alt, Eds. Springer Verlag: Berlin/Heidelberg, 1999.

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